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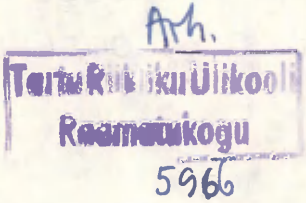

C O N T E N T S

RELATION OF THE HAMMETT EQUATION TO SIMPLE QUANTUM CHEMICAL METHODS

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Existence of a linear free energy relationship may be inferred from quantum chemical principles in an empirical way when calculated quantities are correlated for two series of model compounds with a variable substituent. For example the series of substituted benzoic and cinnamic acids suggest the validity of Hammett equation. Already on the HMO level close correlations were obtained with reasonable values of the slopes, and even some kinds of deviations were indicated, although the values of substituent effects themselves are far from reality. On the CNDO level the latter values are much improved, even the values of ΔE (anion - acid) are acceptable. However, the correlations themselves are not better.

There are many similarities between the correlation analysis, as represented by the Hammett equation, and a simple quantum chemical treatment using static indices. The two kinds of approach were also several times combined or compared. Early work reviewed[1] in 1972, as well as most of the later papers deal with quantum chemical

calculations of substituent effects[2,3] and with comparison to the substituent constants σ, or with the transmission of these effects through various chains[4,5] in relation to reaction constants ρ. This approach contributes merely to the knowledge of individual substituents or reactions, respectively. More important are the attempts[6,7] to derive the general form of the Hammett equation from quantum chemistry, or to show on what assumptions and approximations it is based.

The starting point for both Hammett equation and simple quantum chemical methods is the approximation of the isolated molecule. It means that specific effects of the reagent and solvent are neglected. In further development the two procedures diverge as shown in the following analysis. In the common form of the Hammett equation the constant σ depends only on substituent while the constant ρ involves the effects of side-chain, reaction type, reagent, and conditions. Let us formally resolve the constant ρ into the transmission factor π, dependent only on the side-chain, and the constant ρ° characterizing the reaction:

$$\log (k/k^\circ) = \pi \rho^\circ \sigma$$

The Hammett equation now assumes that the substituent effects are proportional in all reaction series, the individual reaction series differ in the proportionality constant which involves π and ρ° together. The latter two factors need not be in principle separable, i.e. the Hammett equation itself does not require π to be constant for different reactions - this requirement was formulated as an independent principle called the ρ-ρ relation[8]. On the other hand, a simple quantum chemical treatment - say on the HMO level - yields a reactivity index, involving the factors σ and π which are in this case not separable. Hence this approach does not require the same scale of substituent effects for different side-chains. Let us consider the following model

examples in which always two reaction series are compared:

a) Dissociation of various meta- and para-substituted benzoic acids vs the reaction of the same acids with diphenyldiazomethane.

b) Dissociation of various substituted benzoic acids vs dissociation of substituted cinnamic acids with the same substituents.

c) Relative dissociation constants of para-chloro substituted acids with various side-chains vs relative reaction rates of the same acids with diphenyldiazomethane.

The Hammett equation predicts proportionality in the two series a) and b) but not in c), unless the $\rho - \rho$ relation[8] is simultaneously fulfilled. In a quantum chemical treatment the proportionality is required in the cases a) and c), provided the same reactivity index has been used in either series. On the HMO level it has been proved empirically[9] that even different indices are parallel in a broad extent. Another example has been given recently on the SCF-MO level[7]: The Wheland localization energy served as a model of nucleophilic reactivity and the difference of π-electron energies represented the dissociation constant. Several such examples would be able to prove the validity of Hammett equation from the quantum chemistry on empirical principle. However, it has not to be forgotten that the scope of the equation includes still variable side-chains in addition to variable reactions, i.e. also the case b). It is the object of the present paper to show that the Hammett equation can be inferred by a quantum chemical approach even in this case, most important for its general validity. We proceeded again in an empirical way and were interested primarily in the question which simplest method can still yield some relevant results. For this reason we focused attention particularly to the HMO method which

displays some common features with the correlation analysis. The idea of correlating calculated indices for two series of compounds may not be completely new; it was applied e.g. to the basicities of substituted azulenes[10].

As the first example we investigated just the two reactions mentioned under b). In accordance with the general opinion and particularly with reference[7] we preferred to express the substituent effects in terms of energy rather than of charges, although limited correlations of energy and charge are known to exist[11] even beyond the HMO approximation. Hence the dissociation constant was represented by the difference of π-electron energy (ΔE_π) of the anion and acid. Within the framework of the HMO theory a monoatomic substituent on the benzene ring is described by two empirical parameters[12], h_X and k_{CX}, which determine the coulomb integral (α_X) of X and the resonance integral (β_{XC}) of the X-C bond, respectively:

$$\alpha_X = \alpha_C + h_X \beta_{CC}$$

$$\beta_{XC} = k_{XC} \beta_{CC}$$

Instead of choosing suitable values[12] of h_X and k_{XC} for some common substituents, we simply varied these two paramaters within their usual limits. We obtained a series of results some of which correspond closely to certain simple substituents, monoatomic in the sense of the HMO approximation (halogens, CH_3, OH, SH, NH_2). Only the unsubstituted compound is not included. The identity of substituents is not essential for our purpose since we are searching merely for general relationships. The first series was restricted to para substituents because the effect of meta substituents cannot be reproduced correctly by the HMO approach[13].

From the results shown in Fig. 1 the following conclusions can be drawn:

(1) Even the simplest quantum chemical treatment is able to predict the existence of a linear free energy relationship for two series of compounds with a para--substituted benzene ring and two different side-chains. It seems that the approximations inherent in the HMO treatment and in the Hammett equation are similar in character.

(2) By this approach the constant ρ (the slope in Fig. 1) is given a reasonable value, nevertheless it is somewhat higher than the experimental value.

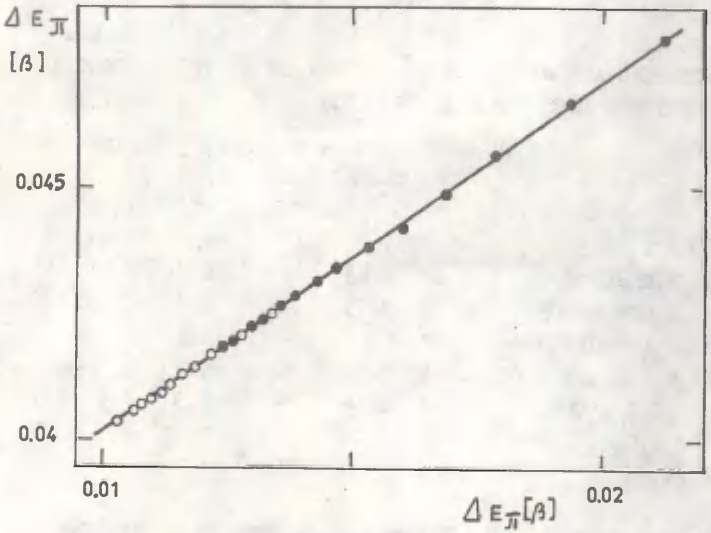

Fig. 1 Prediction of a linear free energy relationship - comparison of HMO π -electron energy differences in the series of para-substituted benzoic acids and cinnamic acids (○ h = 1 to 4, k = 0.4; ● h = 1 to 4, k = 0.7).

In order to verify the above conclusions on more examples, we made similar calculations for further conjugated side-chains, viz. for 5-phenylpentadienoic and biphenyl-4-carboxylic acids. In addition to para series

some meta series were investigated, too. In all cases very accurate linear relationships were obtained. Their slopes are listed in Table 1 and are always higher than the experimental values obtained in water or in mixed aqueous solvents. It is true that these experimental values are sometimes rather uncertain, and if measured in aqueous solvents, they need not correspond exactly to the behaviour of isolated molecules. Yet it seems that the HMO treatment overestimates the transmission of substituent effects through a conjugated chain. Of course,

Table 1

CALCULATED AND EXPERIMENTAL VALUES OF REACTION CONSTANTS ρ FOR THE DISSOCIATION OF ACIDS

Acids	ρ calculated		ρ experimental		(relative)
	HMO	CNDO/2	H_2O	50%(v) EtOH	80%(w) MCS
3,4-RC_6H_4COOH	1	1	1	1	1
4-$RC_6H_4CH{=}CHCOOH$	0.68	0.85	0.42[a]	0.45[b]	0.44[c]
3-$RC_6H_4CH{=}CHCOOH$	0.34	0.59	0.42[a]	0.45[b]	0.44[c]
4-$RC_6H_4(CH{=}CH)_2COOH$	0.50	-	-	0.29[c]	-
3-$RC_6H_4(CH{=}CH)_2COOH$	0.16	-	-	0.29[c]	-
4'-$RC_6H_4C_6H_4COOH$-4	0.21	0.48	-	0.31[e]	(0.45)[f]
3'-$RC_6H_4C_6H_4COOH$-4	-	0.40	-	0.31[e]	-
4-RC_6H_4OH	(~1)	-	2.20[a]	1.77[a]	-

[a] H. van Bekkum, F.E. Verkade, B.M. Wepster, Rec.Trav. Chim. Pays-Bas, 78, 815 (1959); [b] R. Fuchs, J.J. Bloomfield, J.Org.Chem., 31, 3423 (1966); [c] K. Bowden, D.C. Parkin, Can.J.Chem., 46, 3909 (1968); [d] D. Molho, M. Giraud, Bull.Soc.Chim. Fr., 4447 (1969); [e] calculated from the data of T. Drapala, M.J. Malawski, Roczniki Chem., 38, 1593 (1964); [f] in 80%(w) 2-butoxyethanol, valid for para derivatives only, D.J. Byron, G.W. Gray, R.C. Wilson, J.Chem.Soc. C, 831 (1966).

the estimation of ρ's is not the main aim of our approach and can be carried out better by more sophisticated methods[4,5]. As regards the meta substituents, the results have no real significance since the HMO approach neglects the electron repulsion[13]; in terms of organic chemistry it neglects the inductive effect. This failure is not retrieved by introducing the auxiliary inductive parameter[12]. We have included the meta derivatives only for comparison. As expected, their effects are badly underestimated, i.e. by more than one order of magnitude as compared with para substituents. In addition, the direction of the effect is wrong. Surprisingly enough, the linear dependence was quite well fulfilled and the slope

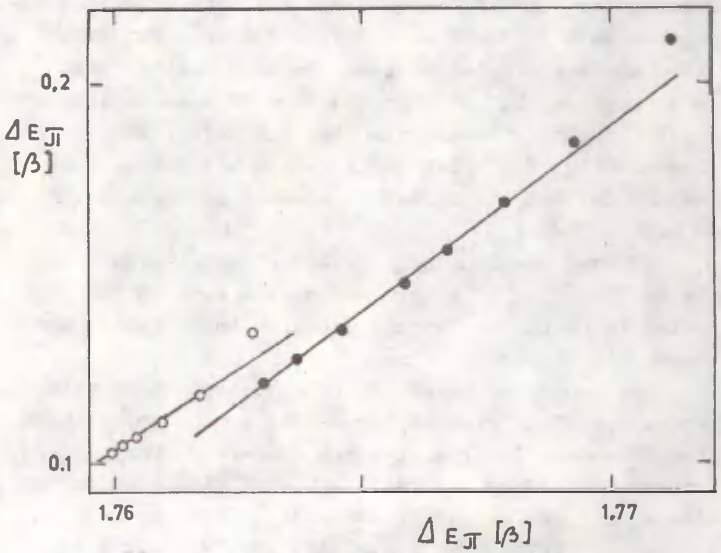

Fig. 2 Restricted validity of a linear free energy relationship - comparison of HMO π-electron energy differences in the series of para-substituted benzoic acids and phenols (○ h = 1 to 4, k = 0.4; ● h = 1 to 4, k = 0.7).

was similar, or even better than that based on para derivatives. We may thus state:

(3) Although the effects of meta substituents are reproduced quite wrongly by the HMO approach, a linear free energy relationship is obtained even in this case.

Note still that the values of ΔE_π themselves have almost no meaning and are not comparable between different acids. They would predict e.g. that the cinnamic acids are much weaker than benzoic acids.

We were further interested whether this very simple treatment is able to indicate even the restricted validity of the Hammett equation and some deviations. Hence we investigated in the same manner the series of para substituted phenols, known for deviations of strong acceptors as well as of some strong donors[1]. The values of ΔE_π are again not comparable between series; they would require that phenols are hundred times weaker acids (in energy terms) than benzoic acids. Nor is the slope in Fig. 2 of much significance but the salient feature is that the linear dependence is violated. Hence we may conclude:

(4) Even the simplest quantum chemical treatment on the HMO level is able to discriminate between reaction series in which the Hammett equation is fulfilled and in which it is not.

The results outlined are of some importance from the general point of view as far as the linear dependences themselves and their slopes are concerned. They do not, however, reproduce the real values of dissociation constants, nor the actual substituent effects because the approach is very primitive. Therefore, we calculated still the differences of energy of all valence electrons (ΔE) on the CNDO level. In this case it is no more possible to deal with idealized substituents but real groups must be investigated with known geometry, including the conformation[14]. This makes difficulties particu-

larly with complex substituents in meta position since assumptions must be made[7] concerning the population of rotamers. For this reason we restricted the calculations to several simple substituents and the results are then somewhat dependent on their selection.

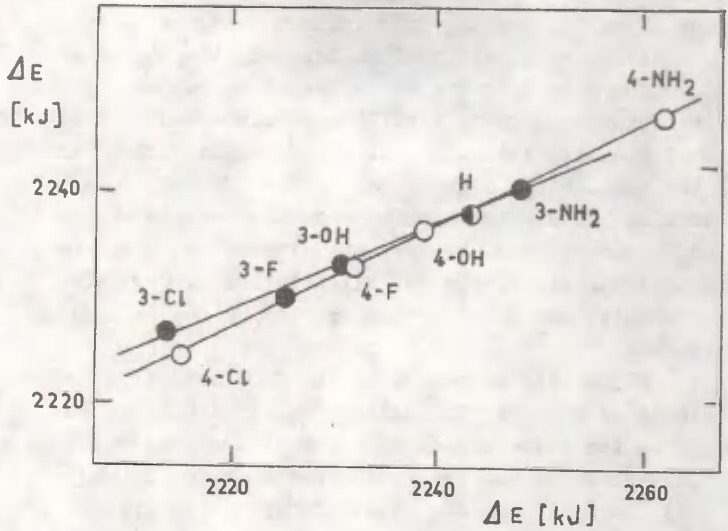

Fig. 3 Prediction of a linear free energy relationship on the CNDO level - plot of the energy differences of all valence electrons concerning meta- and para-substituted benzoic acids and biphenyl-4-carboxylic acids (O para substituents, ● meta substituents).

As expected, our results correspond to real gas phase acidities at least in their order of magnitude, e.g. for benzoic acid calculated 2245, found[15] 1409 kJ mol^{-1}. The substituent effects are also reproduced roughly, e.g. for 4-NO_2 calculated 65.6, found[15] 46.4 kJ mol^{-1}. If only the sequence of substituents is considered, the agreement between theory and experiment is still better (see Fig. 3); the largest deviation is for the 4-OH group which is

in the gas phase more acid strengthening[15] than 3-F. The most important improvement as compared to HMO concerns the relation between meta and para substituents. For example the ratio of substituent effects 4-NO_2 to 3-NO_2 in benzoic acids is calculated to 1.19, found[15] 1.23.

In spite of all this advantages, the CNDO method is not much better for our purposes than HMO. Fig. 3 reveals a good linearity, taking into account that real substituents are under investigation. However, the points of meta and para derivatives are situated on two divergent lines; this phenomenon is still more expressed in the case of cinnamic acids. The slopes given in Table 1 are all too high, still higher than in the HMO method. A very similar picture is observed when the charges on the carboxyl carbon atom are correlated instead of electron energies; the slopes are but slightly lower. Our foregoing results may be thus complemented by the following statements:

(5) Within the framework of the CNDO method the existence of a linear free energy relationship can be predicted for benzene meta and para derivatives with real substituents and for two different side-chains.

(6) The slope of this relationships is somewhat different for meta and para substituents, respectively. In general the transmission through a conjugated side-chain is overestimated by the theory.

In conclusion we may state that even the simplest quantum chemical methods justify the existence of linear free energy relationships for benzene meta and para derivatives, reproduce roughly their slopes, and outline the range of validity. This essential agreement between the correlation analysis and the quantum chemical approach is most striking for the HMO method. It shows that the Hammett equation is also essentially topological in character, although a slight dependence of σ constants on conformation was detected[16].

Calculations: The HMO and CNDO/2 calculations were carried out using standard programs, the latter with originally reecommended parameters and with standard geometry[14].

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STUDY OF S_N1 REACTIONS USING TRIPHENYLVERDAZYLS II. SALT EFFECTS AND Ph_2CHBr IONIZATION MECHANISM IN CH_3CN. NATURE AND ROLE OF SPECIFIC SALT EFFECT

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Ph_2CHBr Ionization kinetics at low substrate conversion degree (~0.1%) in wet CH_3CN (~ $4.5\cdot10^{-2}$ M H_2O) was studied spectroscopically using triphenylverdazyls ($RN^{\cdot}$) with various salts at 25°C. In the presence of $LiClO_4$ and Et_4NClO_4 (0.001-0.1 M) the reaction rate increases (special salt effect), whereas in the presence of N-butylquinolinium iodide (QI), triphenylverdazylium bromide (RN^+Br^-), Bu_4NNO_3, Bu_4NI, Et_4NI, Et_4NBr, Et_4NCl and LiBr (10^{-4}-10^{-3}M) it decreases (negative salt effect) approaching zero with growing salt concentration. In all cases the reaction rate is described by $-d[RN^{\cdot}]/2dt = d[RN^+Br^-]/dt = k_1[Ph_2OHBr]$ being independent of $RN^{\cdot}$ nature and concentration. Perchlorate activity is falling with the increase in salt cation size, and the value of negative salt effect becomes higher with the increase in anion ($Cl^- < Br^- < I^- \simeq NO_3^-$) and salt cation ($Li^+ < Et_4N^+ < Bu_4N^+ < RN^+ < Q^+$) in sizes. t-BuBr Ionization rate in CH_3CN does not depend on the addition of Et_4NBr (~0.001 M), $LiClO_4$ (~0.1 M), and water (~0.1 M). It has been concluded that in t-BuBr case intimate ion pair is formed at the rate-determining step, whereas in Ph_2CHBr case the conversion of intimate ion pair into solvent-separated one is performed via the fast reaction of the latter with $RN^{\cdot}$ and water. Triphenylverdazyls are indicators for solvent-separated ion pairs. Intimate ion pairs do not react with $RN^{\cdot}$, and salt and water additions have little effect on their formation rate as compared with that observed in solvent-separated ion pairs. Winstein's interpretation

of special salt effect was shown to be incorrect. Special and negative salt effects are particular cases of the specific salt effect which consists in the formation of ion triplets between substrate ion pairs and salt ions. ClO_4^- anion catalyzes the conversion of intimate ion pair into solvent-separated pair, whereas other anions and cations stabilyze the intimate ion pair and thus inhibit its conversion into the solvent-separated pair.

The study of salt effects provides a possibility to elucidate details of mechanism of ionization - dissociation process in organic substances (monomolecular solvolysis reactions, S_N1, E1)[1,2]. Ionization rate of carbon - halogen bond in diphenyl methyl halides (solvolysis, S_N1) is very sensitive to the addition of various salts[1-3]. Three types of effects known for these substrates are the following: mass action salt effects (salts with common ion), ionic strength salt effects (salts with non-common ion), and special salt effect (perchlorates). As applied to generally accepted ionization - dissociation pattern (I)

$$\underset{\text{I}}{RX} \rightleftharpoons \underset{\text{II}}{R^+X^-} \rightleftharpoons \underset{\text{III}}{R^+|S|X^-} \rightleftharpoons \underset{\text{IV}}{R^+ + X^-} \qquad (I)$$

the addition of common ion salts brings about the inhibition of dissociation via the increase in the rate in IV⟶III reaction (rate decrease), under the action of perchlorates the anion exchange occurs in III with the formation of $R^+|S|ClO_4^-$ ion pair which is uncapable of converting into an intimate ion pair (reaction rate increase due to the inhibition of external ion pair return III → II) and finally all the salts should increase the rates of I → II → III → IV reactions due to the increase in the solution ionic strength (normal or conventional salt effect). Salts with a non-common ion should, therefore, raise the total reaction rate, whereas for the salts with common ion any overall effect is possible. This conclusion is in good agreement with the available data[1-3]; however, it is not sufficiantly substantiated both theoretically and experimentally.

Salt addition effect on the ionization rate is usually studied at high substrate conversion degrees (>20%). Under such conditions difficulties may arise during the interpretation of experimental results caused by a strong masking effect of the evolving hydrohalide or its salt.

The phenomenon of special salt effect is ill-interpreted. Hughes[4] considered the catalysis of Ph_3CCl methanolysis in benzene by Bu_4NClO_4 additions to be due to ClO_4^- ion effect which, as he puts it, accelerates the substrate ionization to much higher extent than do the ion pairs of this salt. Winstein[5] ascribes $LiClO_4$ catalytic effect in alkyl sulfonate acetolysis to the action of perchlorate ion pair on the solvent-separated ion pair of the substrate. Hammett[2] supports Winstein's interpretation generally accepted at present (external return inhibition) which leads to an incorrect conclusion about the independence of II → III and II → I reaction rates of salt concentration. Gordon doubts Winstein's theory of special salt effect, this fact, however, not preventing him from using it extensively in his review paper[6].

On the basis of studies of Bu_4NClO_4 and Bu_4NCl effect on Ph_3CCl methanolysis rate in benzene and involving the analysis of Hughes' and Winstein's data Leffek[7] concludes that perchlorate effect can be accounted for neither by catalytic effect of ClO_4^- ion, nor by the anion exchange in solvent-separated ion pair. Perrin and Pressing[8] give evidence to favor approximately equal participation of ions and ion pairs in ionization catalysis and dipole stabilization. On this basis they account for the observed phenomenon by the effect of salt ion pair under the special salt effect manifestation (low polarity medium) where practically no perchlorate dissociation occurs[9]. For a large series of solvents the accelerating effect of perchlorate during p-methoxy-neophyltozylate ionization was shown to increase with decreasing solvent polarity[10] and to get lower in acetone solution in the following order: $LiClO_4$ – $NaClO_4$ – Bu_4NClO_4[11]. This indicates the activity of either

ion pairs or of more complex formations.

Interpretation of salt effects is considerably hindered by insufficient knowledge of the effect that III → II → I reactions (external and internal ion pair return) exert on the total (measured) reaction rate. If these reactions compete with the nucleophile, reacting after the rate-determining step, then the rate measured should to some extent depend upon the method of reaction mixture analysis. Up to now it is not yet clear weather salts (ions) with a non-common ion can decrease the rate of II, III, IV - formation (negative salt effect), and the effect of each ion nature (specific salt effect) is also to be clarified. Using the data reported by Clarke and Taft[12], Ingold[1] believes that in t-BuCl hydrolysis specific salt effect is missing. Ref.13 reports specific effects of organic salts ($2\text{-}C_{10}H_7SO_3Na$, Ph_4PCl) during neophyltozylate and 3-phenyl-2-butyltozylate ionization in 50% water solution of dioxane. Gordon[6] believes the decreased values of salt effects in the above case to be due to relative stabilization of substrate over the trasition state.

Negative salt effect (reaction rate decrease after the addition of salts with a non-common ion) was observed previously during the solvolysis of $t\text{-BuONO}_2$ in 60% water solution of dioxane[14], of neophyltozylate in 50% dioxane[13], 1,2-diphenylchloroethane in 70% acetone[15] and of Et_3CCl in 70% acetonitrile[16]. The values of these effects are small (5-25% at salt concentrations of 0.05 - 0.1 M) and may be accounted for by decrease in the substrate activity coefficient[13]. It should be noted that bringing out negative salt effects and elusidation of their nature are of paramount significance for the interpretation of ionization mechanism of organic compounds. Thus, Sneen[17] studing the effect of NaN_3 on secondary sulfonates solvolysis in aqueous dioxane accounts for the change in the reaction rate by the positive salt effect on S_N1 reaction. Schleyer and co-workers[18] consider the Sneen unified mechanism of ion pairs to become doubtful, if the S_N2 reaction takes place

in the above case and NaN_3 reveals negative salt effect.

Previously salt effects on Ph_2CHX ionization rate were predominantly studied in protic solvents and their mixtures with some aprotic ones[1-3]. Information available is unsufficient in many respects. Thus, common ion effect was often determined without any comparison with the effect of other ions[19]. In some cases special salt effect is observed under the action of $Co(NO_3)_2$ whereas $LiClO_4$ leads to a usual salt effect[20]. Information referring to aprotic solvents is scanty. Special salt effect of $NaClO_4$[21] is observed in the reaction of CNS^- ion radioactive exchange in 4,4'-dimethylbenzhydrylthiocyanate in acetone solution, whereas during chlorine anion exchange in p-chlorobenzhydrylchloride in acetone the addition of $LiClO_4$, LiCl and other salts leads to a conventional salt effect[22].

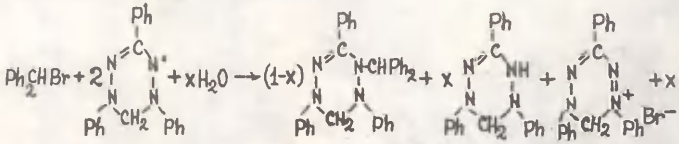
At present salt effects are difficult to predict. Their manifestation depends strongly on salt structure, substrate and reaction conditions which complicates considerably the interpretation of Ph_2CHX ionization mechanism.For these substrates process (I) is usually supposed to proceed to the end (ion formation)[1-3]. This refers both to protic and aprotic solvents. In the latter case a combined mechanism ($S_N1 + S_N2$) is often suggested[19,22,23].

Previous paper[24] reported about monitoring the Ph_2CHBr ionization rate spectrophotometrically using triphenylverdazyls as internal indicators. This method allows to study kinetics at ~ 0.1% substrate conversion. Kinetic studies of Ph_2CHBr ionization in CH_3CN have led to the conclusion that triphenylverdazyls may be used as Ph_2CHX ion pair indicators. The nature of ion pairs in question has not been elucidated.

The purpose of the work is to study salt effects during PH_2CHBr ionization reaction in CH_3CN and to elucidate the mechanism involved. A number of comparative experiments were carried out to specify the effect of various salts and water on t-BuBr ionization rate in CH_3CN.

Results and Discussion

The product-study and kinetic experiments reported in[24] showed that in wet acetonitrile Ph_2CHBr molecule at the rate-determining step converted into an ion pair (intimate or solvent-separated) which further reacts fast with triphenylverdazyl (RN$^{\cdot}$) and water. Hydrogen bromide, evolving in the reaction of the intermediate with water, reacts with RN$^{\cdot}$ by scheme (8). Over-all reaction may be written as follows:



Irrespective of relative amounts of reacting RN$^{\cdot}$ and water one mole of reacted Ph_2CHBr always consumes two moles of RN$^{\cdot}$ (λ_{max} 720 nm, ε=4330) and one mole of triphenylverdazylium bromide (RN^+Br^-, λ_{max}=540 nm, ε=12170) is formed. This provides a means for controlling spectrophotometrically Ph_2CHBr ionization rate. Under these conditions the reaction rate is not affected by the concentration and substituent nature in RN$^{\cdot}$. As elsewhere[24] kinetic experiments were done in CH_3CN containing $\sim 4.5 \cdot 10^{-2}$ M H_2O.

At low conversion rates of Ph_2CHBr ($\sim 0.1\%$) when the salt effect of forming RN^+Br^- is not yet manifested, kinetic equation (3) is valid:

$$-d[RN^{\cdot}] / 2dt = d[RN^+Br^-] / dt = k_1 [Ph_2CHBr] \quad (3)$$

Special experiments showed that at RN^+Br^- concentration in the solution being $\leqslant 2 \cdot 10^{-5}$ M its effect falls within the range of experimental errors, at higher concentrations, however, reaction rate decreases markedly. For this reason experiments with and without salt additions were performed up to RN^+Br^- concentration limit of $2 \cdot 10^{-5}$M. The observed effect of RN^+Br^- might be accounted for by mass action salt effect; a more detailed study of salt effects, however, is contradicting.

The effect of various salts addition on Ph_2CHBr ioniza-

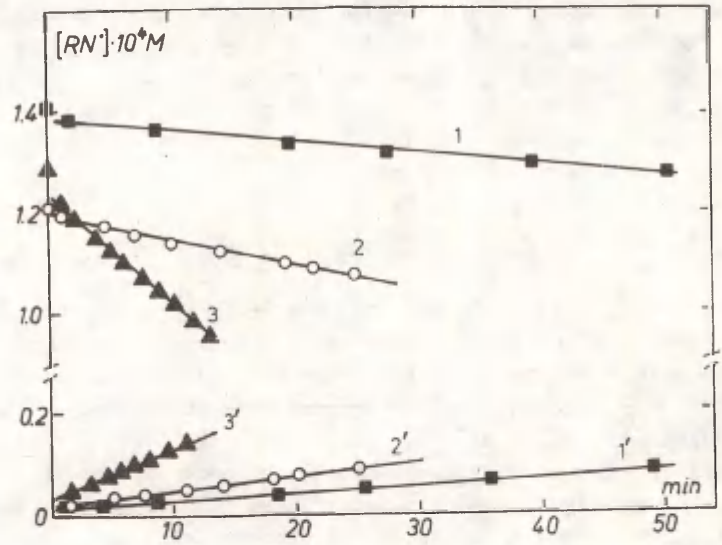


Fig.1. Ph_2CHBr ionization kinetics in the presence of salts, CH_3CN, 25°C

I,I'-$[QI]=1.53\cdot10^{-3}$, $[Ph_2CHBr]=7.78\cdot10^{-3}$M

$k_1=(0.271\pm0.006)\cdot10^{-6}$(against RN·), $k_1=(0.265\pm0.005)\cdot10^{-6}s^{-1}$ (against RN^+)

2,2'-$[Et_4NBr]=1.25\cdot10^{-3}$, $[Ph_2CHBr]=1.04\cdot10^{-2}$M

$k_1=(0.465\pm0.005)\cdot10^{-6}$(against RN·), $k_1=(0.470\pm0.001)\cdot10^{-6}s^{-1}$ (against RN^+)

3,3'-$[LiClO_4]=2.25\cdot10^{-3}$, $[Ph_2CHBr]=5.91\cdot10^{-3}$M

$k_1=(2.95\pm0.01)\cdot10^{-6}$(against RN·), $k_1=(2.95\pm0.05)\cdot10^{-6}s^{-1}$ (against RN^+)

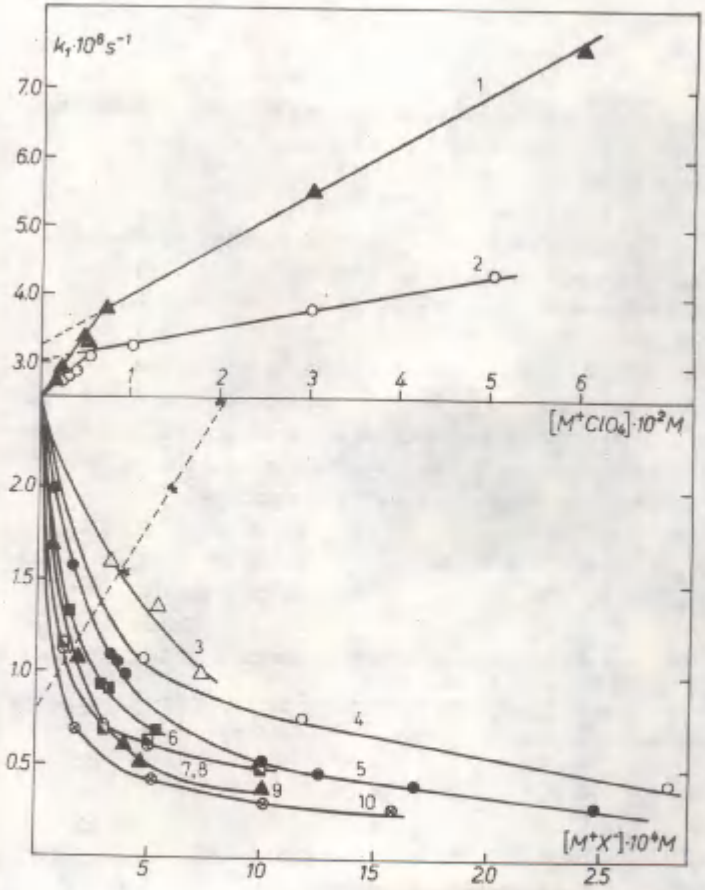


Fig.2. Ph_2CHBr ionization rate coefficient in CH_3CN as a salt concentration function

1. $LiClO_4$
2. Et_4NClO_4
3. Et_4NCl
4. LiBr
5. Et_4NBr
6. Et_4NI
7. Bu_4NI
8. Bu_4NNO_3
9. RN^+Br^-
10. QI

tion rate in acetonitrile was studied. The experiments were done at 25°C with Ph_2CHBr concentration being ~ 0.01M. In all cases the reaction rate is satisfactorily described by kinetic Eq. (3). k_1 Values without salt additions were taken from[24]. Since the experiments were done with 50 to 100-fold excess of Ph_2CHBr over RN° in each individual run the reaction rate was described by zero-order kinetic equation

$$- d[RN^\circ] / 2dt = d[RN^+Br^-] / dt = k_0 \qquad (4)$$

Fig.1 shows some typical kinetic curves for Ph_2CHBr ionization in the presence of various salts. Descending curves indicate RN° concentration fall, whereas ascending ones depict RN^+Br accumulation.

Fig.2 shows the effect of ten different salts on the reaction rate, The salts can be subdivided into 6 different groups. In the first three groups the effect of anion nature is followed, whereas in the remaining three the effect of cation nature is studied (Q-N-butylquinolinium)

1. $LiClO_4$ - LiBr
2. Et_4NI - Et_4NBr - Et_4NCl
3. Bu_4NI - Bu_4NNO_3
4. $LiClO_4$ - Et_4NClO_4
5. RN^+Br^- - Et_4NBr - LiBr
6. QI - Bu_4NI - Et_4NI

Table I

Salt Dissociation Constants and Dissociation Degrees in CH_3CN at 25°C

Salt	k_D, mol/l	$\alpha \cdot 2 \cdot 10^{-4}$ M	References
Et_4NCl	0.003	0.94	25
Et_4NBr	0.052	1.0	26
Et_4NI	0.088	1.0	27
Bu_4NI	0.084 (0.33)	1.0 (1.0)	26 (28)
Bu_4NNO_3	0.14	1.0	29
LiBr	0.0034	0.96	*
QI	0.0046	0.98	*
RN^+Br^-	0.0029	0.93	*
$LiClO_4$	0.029 (0.25)	0.84** 0.98**	30 (31)
Et_4NClO_4	0.017 (0.080)	0.82** 0.94**	32 (33)

* Determined by the authors

** Dissociation degree at 0.005 M

Table I gives salt dissociation constants and degrees at the given concentrations. Under these conditions salts are found entirely or almost entirely as ions.

Perchlorate additions increase the reaction rate, whereas the additions of other salts lead to its decrease, the inhibiting effect being about two orders of magnitude stronger over accelerating. Bromide effects (Group 5) are typical Mass Law salt effects. This fact, however, fails to account for the reaction rate decrease in the presence of salts of a non-common ion (Groups 2, 3, and 6).

Moreover, the growth of inhibiting effect with transition from bromides to iodides and Bu_4NNO_3 indicates that we are dealing here not with mass action salt effect, but with some other kind of phenomenon. This suggests that there occurs no Ph_2CHBr dissociation in acetonitrile, i.e. III $\rightleftharpoons$ IV reactions are of no importance.

In the case studied perchlorate action is typical for so called special salt effect. Indeed, k_1 salt concentration curves for these salts consist of two sections: firstly the reaction rate changes rather fast, and than the flattening of curves is observed. This is a manifestation of two perchlorate effects. Winstain[5,34] and the majority of others[2,3,6,20,35] attribute the first section of the curve to the equilibrium process of $R^+|S|ClO_4^-$ ion pair formation ("cleaning effect")

$$R^+|S|X^- + LiClO_4 \rightleftharpoons R^+|S|ClO_4^- + Li^+X^- \qquad (5)$$

interpreting the second section (after complete anion exchange) as ionic strength salt effect. Fast rate increase along the first section is accounted for by inhibiting the III $\rightarrow$ II reaction. Extrapolation of flat curve sections to zero perchlorate content gives the rate coefficients of $3.2 \cdot 10^{-6} s^{-1}$ ($LiClO_4$) and $3.05 \cdot 10^{-6} s^{-1}$ (Et_4NClO_4). These values are close, the difference between them, however, being considerably beyond the limits of experimantal errors. Values obtained are referred to as the maximum of special salt effect at zero values of usual salt effect. They are approximately 25% (28% for $LiClO_4$ and 22% for Et_4NClO_4)

nigher than k_1 values without salt addition ($2.5 \cdot 10^{-6} s^{-1}$). As shown in Pig.2 other characteristics of special salt effect also depend on cation nature. In Et_4NClO_4 curve deflection occurs at lower salt concentrations (0.005 M). The slope of the second section of Et_4NClO_4 curve is less than that of $LiClO_4$ curve, and b values in Eq.(6) are 8 and 22, respectively

$$k_1^S = k_1(I + \underline{b}[M\ ClO_4]) \qquad (6)$$

To follow Winstein's interpretation of special salt effect, 75% solvent-separated ion pair formed in our case should react with RN· and water, whereas 25% should convert into intimate ion pair (external return). In the presence of difficient perchlorate III → II reaction is completely inhibited and $Ph_2CH^+|S|ClO_4^-$ ion pairs react only with nucleophiles (RN· and H_2O) present in the solution. To put it differently one may suggest a competition between III → II reaction and the reaction of III with nucleophiles without perchlorate addition. This being true, the rate of the reaction measured should depend on that of the reaction following the rate-determining step, i.c. on the rate of interaction between solvent-separated ion pair $Ph_2CH^+|S|Br^-$ and a nucleophile. Consequently the rate constant should increase within $2.5 \cdot 10^{-6}$ and $3.2 \cdot 10^{-6} s^{-1}$ with increasing RN· concentration and growth of its electron donating properties in the substituent series NO_2 - H - CH_3O.

The conclusion based on generally accepted interpretation of special salt effect contradicts to the facts reported in our previous work where it was stated that ionization rate of Ph_2CHBr in CH_3CN was independent of RN· concentration and the nature of its substituent[24]. To confirm this the following measurements were done. Table 2 shows that with three-fold change in RN· concentration k_1 values calculated both by RN· consumption and RN^+Br^--formation vary within the range of experimental errors (Exp. 1-3), $k_1^{av} = (2.54 \pm 0.04) \cdot 10^{-6} s^{-1}$ (previously, $k_1 = (2.50 \pm 0.02) \cdot 10^{-6} s^{-1}$)[24]. In the presence of salts the reaction rate is also independent of RN· concentration. Even more convincing evidence

Table 2

Ph_2CHBr Ionization Kinetics in CH_3CN at 25°C

Exp. No.	$[RN^{\cdot}]\cdot10^4$ M	$[Ph_2CHBr]\cdot10^4$ M	$[Et_4NBr]\cdot10^4$ M	$k_1\cdot10^{-6}s^{-1}$ a)	
				$RN^{\cdot}$	RN^+Br^-
1	0.704	45.7	-	2.38±0.04	2.55±0.05
2	1.57	46.2	-	2.45±0.03	2.59±0.08
3	2.09	46.6	-	2.63±0.01	2.68±0.01
4	1.48	73.6	4.72	0.66±0.01	0.66±0.01
5 b)	1.64	74.5	4.51	0.65±0.01	0.64±0.01
6 c)	1.46	57.5	4.81	0.63±0.01	-

a) Average of two determinations

b) With CH_3O-RN$^{\cdot}$

c) With NO_2-RN$^{\cdot}$

resulted from the analysis of the experimantal data[24] for triphenylverdazyls with substituents in C-phenyl ring (NO_2-RN$^{\cdot}$, H-RN$^{\cdot}$, CH_3O-RH$^{\cdot}$). With transition from NO_2-RN$^{\cdot}$ to CH_3O-RN$^{\cdot}$ the rate of reaction with electrophiles is known to increase by several orders of magnitude[36]. If Winstein's interpretation were true, such change in the nature of the radical would bring about complete inhibition of ion pairs external return and, thus, would increase the rate constant up to $3.2\cdot10^{-6}s^{-1}$. However, this is not observed. In the presence of Et_4NBr ($\sim 4.7\cdot10^{-4}$ M) the reaction rate also does not depend on the radical nature (Exp.4-6). The data obtained in the present paper contradict the interpretation of special salt effect, proposed by Winstein. The mere fact of special salt effect being observed in such highly polar solvents as acetonitrile (ε=37) does not comply with generally accepted views. This effect is usually supposed to be characteristic of solvents with low or medium polarity[1-3]. Thus, it is reported in Ref.10 that in p-methoxyneophiltozilate ionization b values in Eq.(6) for DMSO (ε=49), DMFA (ε=37) and acetone (ε=20) are 0.0, 1.4 and 47, respectively. In our case b is 70 for the first sections of curves. Special salt effect observed in the pre-

sence of $Co(NO_3)_2$[20], LiCl, LiOAc, LiBr and LiOTs[1] also disagrees with Winstein's interpretation. These salts contain anions capable of forming intimate ion pairs and covalent bonds and, therefore, cannot inhibit the external ion pair return. It also should be noted that during cholesteriltozylate solvolysis in CH_3COOH the values of maximum special salt effect at zero level of usual salt effect is considerably dependent on the anion nature, being $33.3 \cdot 10^{-5} s^{-1}$ for $LiClO_4$ and $25.0 \cdot 10^{-5} s^{-1}$ for LiOTs (50,2°0). The cation nature was also shown to be of importance.

Ingold does not accept the formation of various types of ion pairs during RX[1] ionization. He considers the special salt effect to be linked with $R^+Y^-M^+Y^-$ quadrupole formation (rapid equilibrium stage) which then slowly rearranges into $R^+Y^-M^+X^-$ quadrupole. Rearrangement rate is supposed to be close to ionization rate of HX. If RX ionization is rate-determining, S_N1 reaction occurs, if, however, the rate is determined by quadrupole rearrangement, $S_N2(0^+)$ reaction is observed. Ingold believes that special salt effect is an evidence of an intermediate mechanism. In other works, Ingold's interpretation implies that the interaction of substrate ion pair with nucleophile can affect the overall reaction rate. Ingold's interpretation avoids certain contradictions, e.g., the dependance of maximum special salt effect level on salt nature, but as the Winstein's, it contradicts to our data, reporting that overall reaction rate is independent of verdazyl concentration and nature.

Thus available explanations of special salt effect in organic ionization reactions are poorly grounded and fail to interprete our data on Ph_2CHBr ionization in CH_3CN. The necessity of a new approach is evident. Attempting to find such an approach we compared the effects of salt and water additions on Ph_2CHBr and t-BuBr ionization rates under similar conditions. It is supposed that at the rate-determining step of the latter reaction t-BuBr is ionized with the formation of an intimate ion pair, which later

either rapidly eliminates of the hydrogen bromide (E1) or reacts with the nucleophile (S_N1). The above being true, the effects of salt and water in this case should be attributed to their influence on I $\rightleftharpoons$ II reactions.

Kinetic study of t-BuBr ionization in CH_3CN using triphenylverdazyl radicals was reported earlier [37]. In this case RN$^\bullet$ reacts rapidly and quantitatively with HBr formed after the rate-determining step (intimate ion pair formation)

$$t\text{-BuBr} \rightleftharpoons t\text{-Bu}^+\text{Br}^- \rightleftharpoons CH_2{=}CMe_2{+}HBr \qquad (7)$$

$$2RN^\bullet{+}HBr \longrightarrow RN^+Br^-{+}RNH \qquad (8)$$

Similar to Ph_2CHBr ionization the reaction rate is described by the following equation:

$$-d[RN^\bullet]/2dt = d[RN^+Br^-]/dt = k_1[t\text{-BuBr}]. \qquad (9)$$

It should be noted here that RN$^\bullet$ in this case reacts only with HBr, rather than with an intermediate ion pair. The above is confirmed by satisfactory agreement between t-BuBr ionization rates calculated from titrimetric data[38,39] and those obtained from RN$^\bullet$ concentration changes [37,40] both for acetonitrile and acetone. It may be assumed, therefore, that triphenylverdazyls do not react with intimate ion pairs.

No study of the effect of salt and water additions on t-BuBr ionization rate in CH_3CN was yet reported. Table 3 shows our measurements of t-BuBr ionization rate. The test procedures were as in[37]. As shown in the Table, Et_4NBr, $LiClO_4$, and H_2O additions at the concentrations used exert practically no effect on the rate of this reaction: average $k_1^{25°C}$ is $(1.19 \pm 0.02)\cdot10^{-6}s^{-1}$; previously, in[37], $k_1^{25°C}$ was $(1.25 \pm 0.02)\cdot10^{-6}s^{-1}$. Under similar conditions 5 to 10-fold decrease in Ph_2CHBr ionization rate is observed in the presence of Et_4NBr, whereas in the presence of $LiClO_4$ and water the rate increased 2 to 3 times and 1.3 times, respectively. These comparisons make evident different nature of transition states during Ph_2CHBr and t-BuBr ionization. With t-BuBr the lack of common ion salt effect suggests that no substrate dissociation should occur, where-

Table 3

Kinetics of t-BuBr Ionization in CH_3CN at 25°C

[t-BuBr] M	$[RN^+]\cdot10^4$ M	Additions		$k_1\cdot10^{-6}s^{-1}$ ≡)	
		Nature	M	RN^+	RN^+
0.170	1.85	-	-	1.17±0.02	1.19±0.01
0.064	1.85	Et_4NBr	$7.8\cdot10^{-4}$	1.25±0.04	1.21±0.06
0.067	1.85	Et_4NBr	$4.7\cdot10^{-3}$	1.17±0.04	1.11±0.01
0.065	1.82	$LiClO_4$	$2.0\cdot10^{-2}$	1.17±0.01	1.07±0.04
0.065	1.82	$LiClO_4$	$4.9\cdot10^{-2}$	1.09±0.02	1.13±0.05
0.063	1.71	$LiClO_4$	$5.7\cdot10^{-2}$	1.24±0.015	1.19±0.01
0.063	2.22	H_2O	$5.2\cdot10^{-2}$	1.23±0.01	1.26±0.01
0.060	2.22	H_2O	$7.4\cdot10^{-2}$	1.29±0.01	1.26±0.01

k_1 av. = $(1.19\pm0.02)\cdot10^{-6}s^{-1}$

≡) Average of two determinations

as the absence of $LiClO_4$ special salt effect opposes the intermediate formation of solvent-separated ion pair. Thus, during t-BuBr ionization the formation of an intimate ion pair is observed at the rate determining step. Assuming that with Ph_2CHBr the formation of intimate ion pair is also only slightly affected by water and salt additions, we may conclude that during the ionization of this substrate the intimate ion pair ie converted into the solvent-separated one at the rate determining step. As shown above, no Ph_2CHBr dissociation in CH_3CN is observed. Perchlorate effect may be either due to the acceleration of II→III reaction or due to the reverse process inhibition. The latter has been shown not to occur, therefore perchlorates catalyze the convertion of the intimate ion pair into the solvent - separated one.

Under our conditions $LiClO_4$ and Et_4NClO_4 are present mainly in ion form (Table I). If following the assumption of[8] we also assume that ions and ion pairs are approximately equal in their catalytic activity in ionization; then it would appear that in our case catalysis is performed by ions rather than by perchlorate ion pairs. Comparison of

$LiClO_4$ and LiBr effects (slight rate increase and sharp rate decrease, respectively) suggests that ClO_4^- anion should be responsible for catalytic effect. Li^+ cation seems to exert weak or no effect on the rate of this reaction. Thus, Ph_2CHBr ionization rate was found to be practically unchanged in the presence of $\sim 3 \cdot 10^{-4}$ M $LiClO_4$. The same concentration of LiBr causes approximately 2-fold decrease of the reaction rate.

As shown in Fig.2 all the salts (with the exception of perchlorates) slow the reaction down. Negative salt effect is increasing in the following order (10):

$$\underset{1.3}{Et_4NCl} < \underset{1.5}{LiBr} < \underset{1.9}{Et_4NBr} < \underset{2.1}{Et_4NI} < \underset{2.6}{RN^+Br^-} \simeq \underset{2.6}{Bu_4NI} \simeq \underset{2.6}{Bu_4NNO_3} < \underset{3.4}{QI} \quad (10)$$

Numbers below represent the quotients of rate constants without salts divided by those at salt concentration of $2 \cdot 10^{-4}$ M. Already at this concentration value QI decreases Ph_2CHBr ionization rate more than three times. The inhibiting effect is growing with the concentration: in the presence of $1.55 \cdot 10^{-3}$ M QI 9-fold decrease in the rate is observed with the 13-fold drop corresponding to 0.05 M of Et_4NBr ($k_1 = 0.20 \cdot 10^{-6} s^{-1}$). Observed relationship between reaction rates and salt concentration is non-linear as plotted in k_1 - [MX] coordinates. The above relation can be approximated neither by k_1 - lg [MX] ($\sqrt{[MX]}$, $[MX]^2$) nor by lg k_1 - [MX] (lg [MX], $\sqrt{[MX]}$, $[MX]^2$) functions which proves the complexity of the phenomenon in question. Unfortunately we didn't manage to test salt concentrations sufficient for complete Ph_2CHBr ionization inhibition. Bromides have low solubility in CH_3CN, whereas iodides react with RN^+Br^- at concentrations higher than $1.6 \cdot 10^{-3}$ M. During k_1/salt concentration relationship study in no case we observed either saturation effect or k_1 passing through the minimum. This permits to assume that reaction rates asymptotically approach zero with increasing concentration.

Negative salt effect is increasing in the following series with the increase in sizes of anion (11) and cation (12)

$$Cl^- < Br^- < I^- \simeq NO_3^- \quad (11)$$

$$Li^+ < Et_4N^+ < Bu_4N^+ < RN^+ < Q^+ \quad (12)$$

LiBr case suggests that negative salt effect should be attributed to the action of the anion. Observed cation nature effects show that the cation also contributes into the process. The amount of this contribution is increasing according to series (12) with the first member of the series having almost no effect on the reaction rate. In this connection it should be noted that the growth of negative salt effect with the increase in salt ion size suggests the ions being active rather than ion pairs since the efficiency of quadrupole interaction observed with ion pairs is known to increase with the decrease in ion sizes in ion pairs[2,41]. Negative salt effect of cations is also evidenced by the fact, that in the presence of Et_4NClO_4 the reaction rate increases less than with $LiClO_4$. This observation is linked with partial decrease in reaction rate caused by Et_4N^+, this decrease being in any case greater than that caused by Li^+. This conclusion is in good agreement with the observed growth of negative salt effect in cation series (12). Observed perchlorate salt effect is represented by the difference between two values, that of rate increasing anion effect, on one hand, and rate decreasing cation effect, on the other. Special salt effect may be observed only at dominating anion effect. If ion effects are equal in amount, usual salt effect will be observed.

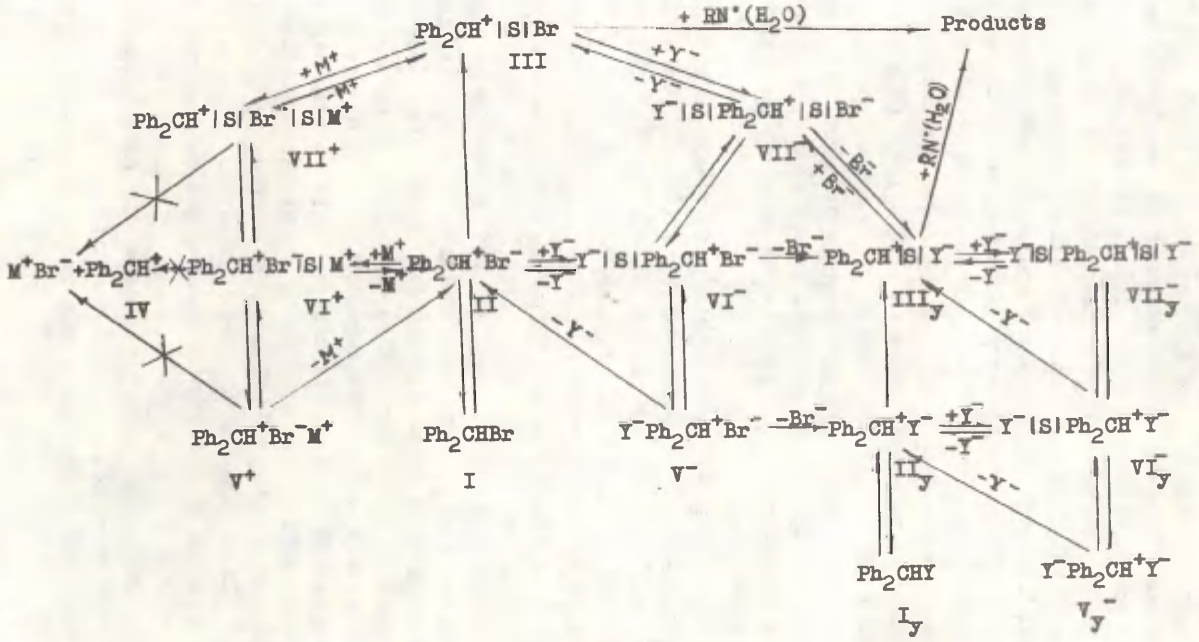
Having compared salt effects on t-BuBr and Ph_2CHBr ionization rates, we came to the conclusion that salt effects during Ph_2CHBr ionization are related to the ion effect on II $\rightleftharpoons$ III reactions rates. With negative salt effects salt ion (mainly, salt anion) either decreases the rate of intimate ion pair conversion into solvent-separated one or catalyzes the reaction of external return. If in the presence of salt III$\longrightarrow$II reaction grew and became competative for reaction III+RN$^-\longrightarrow$ products, overall

reaction rate would depend on RN$^{\cdot}$ concentration and nature. In the presence of Et_4NBr the Ph_2CHBr ionization rate was shown to be independent of RN$^{\cdot}$ concentration and the nature of its substituent (Table 2). The negative salt effect, therefore, is connected with the action of ions on II → III reaction. This salt effect represents combined contribution of salt anion and cation acting in the same direction. This effect is superimposed by the usual salt effect. The value of the latter may be obtained from the experiments with $LiClO_4$. Fig.2 shows the reaction rate to increase more than twice at $[LiClO_4]$ = 0.05 M due to usual salt effect. At $[Et_4NBr]$ = 0.05 M approximately 13 times decrease in the reaction rate is observed. Comparative analysis of the values obtained proves consideranle contribution of ionic strength effect to the negative salt effect under observation.

The data obtained by the authors can be summarized as follows: ClO_4^- anion accelerates II⟶III reaction, whereas the rest of both anions (Cl^-, Br^-, I^-, NO_3^-) and cations reduce it. There are all reasons to suggest that both effects should manifest themselves as a result of the ion action on the intimate ion pair. An ion triplet is formed[2,6,42] which can be formed in the solution also at very low concentrations (app. 10^{-3}M)[6]. Formation of triplet intermediates in one case catalyzes II → III reaction, inhibiting it in another. This conclusion is not unexpected, since an ion can stabilize the dipole of either initial or transition state. The formation of triplets from solvent-separated ion pairs is also worth to be considered. With due regard of all said above Ph_2CHBr ionization mechanism in the presence of salts may be written as in (13).

In the absence of salts ionization proceeds up to the formation of a solvent-separated ion pair at rate determining step (I ⇌ II → III), which reacts with nucleophiles (RN$^{\cdot}$, H_2O) as it appears. The rate of the latter reaction is so high, that the external return can be neglected. Salt additions are accompanied by ion trip-

Scheme 13


Ph2CH+ | S | Br
III
+ RN+(H2O)
Products
+M+
-M+
+Y-
-Y-
Ph2CH+ | S | Br- | S | M+
VII+
Y- | S | Ph2CH+ | S | Br-
VII
-Br-
+Br-
+RN+(H2O)
M+Br- + Ph2CH+
IV
Ph2CH+Br- | S | M+
VI+
Ph2CH+Br-
II
Y- | S | Ph2CH+Br-
VI-
Ph2CH+ | S | Y-
IIIy
Y- | S | Ph2CH+ | S | Y-
VIIy-
Ph2CH+Br- M+
V+
Ph2CHBr
I
Y-Ph2CH+Br-
V-
Ph2CH+Y-
IIy
Y- | S | Ph2CH+Y-
VIy-
Ph2CHY
Iy
Y-Ph2CH+Y-
Vy-

let formations. Since ions and ion pairs in the solution are solvated, the interaction of these particles is expected to give solvent-separated triplets of VI and VII type which similar to intimate ion pairs do not react with RN$^{\cdot}$ or water. Strong charge delocalization seems to be the reason. Since the rate of triplet formation is diffusion - controlled[6], only equilibrium state II $\rightleftharpoons$ VI, III $\rightleftharpoons$ VII, $II_y^- \rightleftharpoons VI_y^-$, $III_y \rightleftharpoons VII_y^-$, $III_y \rightleftharpoons VII^-$ is critical for our case (thermodynamic control). Equilibrium state is also significant for reactions I $\rightleftharpoons$ II, $I_y \rightleftharpoons II_y$ (substrate conversion into intimate ion pairs) and VI $\rightleftharpoons$ VII, V $\rightleftharpoons$ VI, $V_y^- \rightleftharpoons VI_y^-$, $VI_y^- \rightleftharpoons VII_y^-$ (triplet mutual conversion) in this case, however, the equilibrium state is slowly established. Reactions II $\rightarrow$ III, $II_y^- \rightarrow III_y$ (conversion of intimate ion pairs into solvent-separated ones), $VI^- \rightarrow III_y$, V $\rightarrow$ II, $V^- \rightarrow II_y$, $V_y^- \rightarrow II_y$, $VI_y^- \rightarrow III_y$ (triplet dissociation) are irreversible. For the first two reactions this fact is related to fast reaction of the forming product with nucleophiles. In the latter four cases no reverse reaction mechanism is available. For $VI^- \rightarrow III_y$ reaction both explanations are true.

As shown in (13) negatively charged partially solvent separated triplets VI^- formed from the intimate ion pair may disintegrate forming initial ion pair II, convert into the intimate triplet V^- (solvent extrusion) and form solvent -separated ion pair III_y and completely solvent-separated triplet VII^-. Solvent-separated ion pair III_y similar to III rapidly reacts with nucleophiles (RN$^{\cdot}$ and H_2O) in the solution. In ClO_4^- case no intimate ion triplet is formed as well as no VII_y^- conversion into VI_y^- is observed and for that reason II_y, I_y and V_y^- are not formed. Some acceleration observed in this case may be connected only with $VI^- \rightarrow III_y$ reaction. It is at this stage primary stabilization of transition state by OIO_4^- anion is observed. Reactions $III_y \rightarrow VII^-$, $III_y \rightarrow VII_y^-$, III $\rightarrow VII^-$ (triplet formation from solvent-separated ion pairs) and $VI^- \rightarrow VII^-$ may only decrease the overall reaction rate. At low perchlorate con-

centrations, when $II \rightleftharpoons VI^-$ equilibrium is not yet completely shifted to the right, II $\rightarrow$ III reaction also proceeds partly. When perchlorate concentration reaches the level providing for practically complete conversion of II into VI, further formation of the reaction products occurs via the path of $I \rightarrow II \rightarrow VI^- \rightarrow III_y$ / $\rightarrow VII^- \rightarrow III_y$. The formation of VII_y^- from III_y and that of VII^- from VI^- and III_y seems to inhibit this process to certain extent. However, the reactions proceed along the mentioned path with higher rate, than it is observed without perchlorate addition by mechanism $I \rightarrow II \rightarrow III$. With due account of rate-decreasing cation effect overall reaction rate increases by 22% and 28% for Et_4NClO_4 and $LiClO_4$, respectively. Thus ClO_4^- catalytic effect is reduced to nucleophilic anion substitution in the intimate ion pair which following this process is converted into the solvent-separated one. Consequently our explanation as well as in Winstein's interpretation is based on the intermediate formation of the solvent-separated ion pair, containing ClO_4^- anion. As opposed to Winstein, however, we believe that it results in acceleration of the intimate ion pair conversion into the solvent-separated one, rather than external return inhibition.(* This considerable difference is essential for the understanding of salt effects observed in solvolysis and S_N1 reaction.

In the formation of negatively charged triplets from other anions $VI^- \rightarrow III_y$ reaction seems to have no critical value. This is suggested by Ph_2CHBr ionization rate approaching zero with the increase in salt concentration. The same approach allows to consider that reactions $VII^- \rightarrow III_y$, $II_y \rightarrow III_y$ and $VII_y^- \rightarrow III_y$ do not proceed, at least, for Cl^-, Br^-, I^- and NO_3^- anions.

(*This reaction, if any, is inhibited by rapid subsequent reactions between III and nucleophiles.

In this case the main result of triplet formation will be in the fall of II concentration and thus in the inhibition of $II \rightarrow III$ reaction. In fact the formation of VI^- may be regarded as a stabilization process of the initial ion pair II (ion triplet formation decreases the energy of the system[2,6]). Stabilizing salt effect should increase due to equilibrium conversion of VI^- into VII^- and V^-. Intimate anion triplet V^- may undergo further transformations, i.e. decompose forming initial ion pair II and ion pair II_y. The latter pair may be trapped by covalent product I_y (anion exchange) transform into III_y or convert into partial solvent separated triplet VI_y^-, which may be either in equilibrium with ion triplets VII_y^- and V_y^- or disintegrate, forming II_y or III_y. I_y accumulation might lead either to acceleration ($y = NO_3^-$, I^-) or inhibition ($y = Cl^-$) of the overall reaction rate due to atterations in the substrate nature. In our case when substrate conversion is approximately 0.1% anion exchange effect in Ph_2CHBr remains unnoticable. The increase in this effect in anion series (11) confirms the above. Reactions $II_y \rightleftharpoons VI_y^- \rightleftharpoons V_y^- \rightarrow II_y$ and $VII_y^- \rightleftharpoons VI_y^- \rightarrow III_y$ also have no effect on the rate at low substrate conversion. Thus we may conclude that the negative salt effect of anions is determined by $II \rightleftharpoons VI^- \rightleftharpoons VII^- \rightleftharpoons V^-$ (initial ion pair II stabilization due to its conversion into negatively charged triplets)

Cation action (Eq.(13), left side) also may be interpreted in terms of initial state II stabilization. In this case initially forming solvent-separated triplet VI^+ may convert into completely solvent-separated triplet VII^+ and intimate triplet V^+. No dissociation of these triplets with Ph_2CH^+ formation is observed.

Thus, salt effects observed in our case are related to the availability of $II \rightleftharpoons VI$ equilibrium. Anion ClO_4^- is a weaker complex-forming agent, than other anions, therefore perchlorate salt effect manifests itself at much higher concentrations than others. Indeed the inhibition of negative

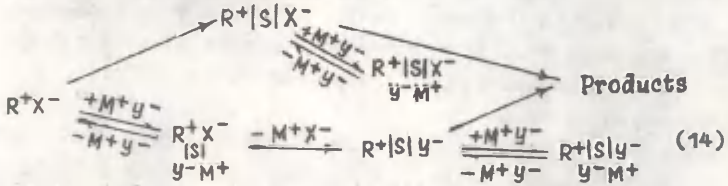
salt effect of $48 \cdot 10^{-4}$M Et_4NBr ($k_1 = 0.73 \cdot 10^{-6} s^{-1}$) requires 45 times more of $LiClO_4$ ($2.1 \cdot 10^{-3}$M, $k_1 = 2.48 \cdot 10^{-6} s^{-1}$). Dashed line in Fig.2 shows the effect of $LiClO_4$ addition (upper abscissa) on Ph_2CHBr ionization rate ($\sim 8 \cdot 10^{-3}$M) in the presence of Et_4NBr ($4.8 \cdot 10^{-4}$M). A weaker salt effect of cations as compared with that of anions seems to be connected with the fact, that $II \rightleftharpoons VI$ equilibrium shift to the right is greater in the latter case. Nevertheless cation contributes largely into the observed salt effects. This is shown by considerable growth of salt effect in cation series (12). Under the conditions of special salt effect cation contribution is made evident by the rightward shift of $II \rightleftharpoons VI^+$ equilibrium between $LiClO_4$ and Et_4NClO_4. This results in complete bonding of II in VI^- and VI^+ (deflection point of $k_1 - [Et_4NClO_4]$ curve) at lower salt concentrations as well as in the decrease in maximum special salt effect value (from $3.2 \cdot 10^{-6}$ to $3.05 \cdot 10^{-6}$). Less steep slope of the second part of Et_4NClO_4 curve as compared with $LiClO_4$ case suggests that with the increase in the solution ionic strength the stabilizing cation effect should grow alongside with the $VI^- \longrightarrow III_y$ reaction rate, this effect being greater for Et_4N^+ than for Li^+. This may be attributed to the increase in $VI^+ \longrightarrow VII^+$ reaction rate.

Increasing negative salt effect with the increase in salt ion size may be interpreted in terms of hard and soft acids and bases. It seems natural to suppose that ion pairs are softer acids and bases than free ions. Ion triplet forming capacity should therefore increase with the decrease in hardness of bases (anions) and acids (cations). This fact is confirmed experimentally.

The study of salt effects nature during Ph_2CHBr ionization in CH_3CN indicates that we deal here with the local action of ions, which, as opposed to ionic strength salt effect, depends strongly on the nature of both anion and cation, that is a specific interaction between ions and ion pairs. Negative and special salt effects observed in our case may, therefore, be regarded as particular cases of the specific

salt effect which is of much more significance, than it was supposed previously[1,6] . It may take any form known for salt effects. The above explains difficulties met during its identification which was shown earlier taking special salt effect as an example.

Our interpretation of specific salt effect is based on the action of ions, rather than that of salt ion pairs. This approach is sufficiently justified by the level of salt dissociation and the effect of ion size. It should be noted that not only Hughes[4], but also Leffek[7] and Winstein in his early works[43] believed that at low salt concentration anion ClO_4^- has catalytic activity. Under different conditions and, perhaps, in our case also specific salt effect may be related to salt dipole effect on substrate ion pairs. With this our basic approach is the same: perchlorate dipole via intermediate quadrupole catalyzes intimate ion pair conversion into the solvent-separated one, whereas other salts stabilize the intimate ion pair to the extent (stronger or weaker) of the solvent-separated one. This process may be represented as



(14)

Gordon believes that anion exchange in an ion pair may proceed both via intermediate quadrupoles and ion triplets. However, the role of quadrupole interaction in the ionization reactions of organic substrates is not yet clearly understood. The increase in salt effects with decreasing medium polarity and salt dissociation degree does not prove as yet that the salt ion pair is an active agent. In this case the reaction may proceed through ion triplet type VI intermediate:

$$R^+X^- + Y^-M^+Y^- \xrightarrow{-M^+Y^-} Y^- |S| R^+X^- \xrightarrow{-X^-} R^+ |S| Y^- \quad (15)$$

It should be noted that we could identify and inter-

prete the salt effects found only under the condition of very low substrate conversion quantity. Already at 1% substrate conversion the picture of salt effects would be greatly distorted and would become difficult to be interpreted. Fig.2 illustrates the above.

Catalytic effect of water on ionization rate may be interpreted in terms of the mechanism proposed by the authors having assumed that both water and salt additions had greater effect on II → III than on I → II. Linear increase in ionization rate in a polar solvent with the increasing water concentration of small water amounts may serve as an indication of the intermediate formation of III. In the case of intermediate formation of solvent-separated ion pairs the reaction rate in protic solvents should greately increase. Indeed, Ph_2CHBr ionization rate increases 6000 times between CH_3CN and CH_3OH, whereas for t-BuBr (intimate ion pair formation) only 25 times increase is observed[44].

While interpreting salt effects during Ph_2CHBr ionization we assumed that triphenylverdazyls reacted only with solvent-separated ion pairs and the rate of this reaction is so high that external return is completely inhibited. If the opposite were true, the reaction rate control method would be unsatisfactory. The second critical point is that the triphenylverdazyl does not react at all with intimate ion pairs. Otherwise the overall reaction rate would depend on radical nature and concentration due to the inhibition of II → I reaction. Thus we approach the conclusion that triphenylverdazyls are the indicators of solvent-separated ion pairs.

Proposed interpretation of special salt effect as a particular case of specific salt effect allows us to explain the experimental data obtained.

1. Depending upon the conditions involved this effect may be induced both by ions and salt ion pairs. With our approach it is a more specific point.

2. This effect may appear not only under the action of perchlorates, but also of other salts. It depends on the

relation between the rates of $VI^- \rightarrow III_y$ and $II \rightarrow III$ reactions (Eq.13). In our case for halides and nitrates the rate of $VI^- \rightarrow III_y$ reaction is very low. Under different conditions, however, it may be higher than that of $II \rightarrow III$ reaction for these and other anions, different from the perchlorates. The lack of perchlorate special salt effect may be related to the fact that the rates of both reactions are close. 28 and 22% difference observed in our case suggests that this may be realized.

3. Maximum value of special salt effect at zero level of the usual one should depend on the salt nature, since it is determined by the action of salt anions (ion pairs) on II and III reactions, rather than by the inhibition of external return.

4. Effect observed in a polar solvent is related to the catalytic action of ClO_4^- anion, rather than salt ion pair. Decreasing value of the effect with the increase in the solvent polarity may be due to the leftward shift of $II \rightleftharpoons VI^-$ equilibrium.

5. Our method gives no information on the internal ion pair return. Published information favors the reaction $II \rightarrow I$. Thus the rates of substrate racemization[34], scrambling[18] of O in p-chlorobenzhydride-n-nitrobenzoate[45] and anion fragmentation in $Ph_2CHOOSOH_3$[46] are higher than those of anion exchange reactions in the substrate. The formers are supposed to proceed through intimate ion pairs, whereas the latters are suggested to occur via solvent separated ones. As shown by Eq.(13) anion exchange in an intimate ion pair may proceed through intermediate ion triplets.

6. We can easily answer Gordon's questions[6] arising from the discussion of Winstein's interpretation.

a) He believes that it is hard to make out what results from $ClO_4^- |S|R^+|S|X^-$ which explains the elimination of the return. The formation of similar triplets (VII^- and VII_y^-) was discussed earlier and shown by Eq.(13).

b) Gordon asks in what way ClO_4^- causes racemization in the system if no reaction of intimate ion pairs with ClO_4^- dur-

ing 2-octyltozylate[47] acetolysis to cause special salt effect is observed. Eq.(13) shows ClO_4^- to react with the intimate ion pair. The lack of special salt effect may be attributed to the fact that either the rates of II → III and $VI^- \rightarrow III_y$ reactions are close or anion accelerating and cation inhibiting effects make up for one another.

c) Gordon's answer to his previous question is that exchange equilibrium constant in an intimate ion pair is lower than in a solvent-separated one and wonders why K value for intimate ion pairs is small whereas for solvent separated ones it is large and, therefore, characterized by a special salt effect. We believe that intimate ion pairs form triplets (quadrupoles) easier than solvent-separated ones, thus providing for an increase in the reaction rate in the presence of perchlorates.

Experimental

Pure Ph_2CHBr, triphenylverdazyls and CH_3CN were obtained as in[24]. Triphenylverdazylium bromide was obtained as in[48] and Et_4NClO_4 as recommended by[32]. Bu_4NNO_3 was prepared by the reaction of Bu_4NI with $AgNO_3$. N-butylquinolinium iodide was prepared from quinoline and BuI[49]. All other salts are commercial products. Pure reagents were stored in dessicator over P_2O_5. Salt dissociation constants were determined by the Kraus-Brey method[50]. Kinetic tests were done as in[24].

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STRUCTURE OF AMINES AND MECHANISM OF THEIR REACTIONS WITH VINYL HALIDES

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The kinetics of interaction of trans-p-nitrophenyl-β-chlorovinylsulfone with different classes of amines (primary, secondary, and tertiary) is studied in chlorobenzene at 25°C. The rate constants of the process are shown to be described by the equation $\lg k = \lg k_0 + \rho^{*}\sigma^{*} + \delta E_N$ for all amines studied. A single correlation dependence for the reactions studied is obtained. On this basis the conclusion is made that different classes of amines interact with trans-p-nitrophenyl-β-chlorovinylsulfone via the same mechanism.

Mechanism of nucleophilic substitution in the series of vinylhalogen compounds is at present a subject of systematic studies, which is accounted for by wide spreading of such processes in chemical practice[1]. The vinyl halides with activating groups capable of forming intramolecular hydrogen bonds (IHB) with proton containing nucleophiles in the intermediate (or in the transition state closely related to it structurally) are of special interest. To those belong, e.g., β-halogenvinyl ketones whose reactions with primary and secondary amines occur via cyclic transition state where IHB is formed between carbonyl and hydrogen atom of amino group[2,3]. Naturally, interactions of these substrates with tertiary amines without a hydrogen atom at nitrogen proceed through another transition state and, hence, obey other regularities[3].

It was of interest to elucidate whether the above differ-

ences are still present in the reaction mechanisms involving amines of different classes with transition from β-halogenvinyl ketones to the closely related to them structurally compounds, such as β-halogenvinyl sulfones. With this purpose we studied the reaction of trans-p-nitrophenyl-β-chlorovinylsulfone with alkyl amines with different structure (primary, secondary, and tertiary) in chlorobenzene* at 25° (Table 1). It was found (see also Refs. 6 and 7) that the interaction with primary and secondary amines proceeded according to stoichiometric equation (1) and with tertiary amines by scheme (2).

$$ArSO_2CH{=}CHCl + 2R_1R_2NH \longrightarrow ArSO_2CH{=}CHNR_1R_2 + R_1R_2\overset{+}{N}H_2 \cdot Cl^- \quad (1)$$

$$ArSO_2CH = CHCl + R_1R_2R_3N \longrightarrow ArSO_2CH = CHNR_1R_2R_3\overset{+}{N} \cdot Cl^- \quad (2)$$

In the case of secondary and tertiary amines the reaction rate** is described by the standard second order equation (first order on each reagent). As for reactions of ammonia and primary amines, the bimolecular process is paralleled here by another one catalyzed by the second molecule of an initial amine (spontaneous catalysis). This is manifested by the fact that without changing during the process (with high excess of amine concentration over that of vinyl sulfone) the observed second order rate constants ($k_{obs.}$) grow regularly with the increase in the initial amine (reagent (b)). In this case the rate constants of the non-catalytic (k) and catalytic (k_b) processes were found from

*For synthesis and purification of the compounds needed see Refs. 4 and 5.

**The reaction was monitored analytically by determining the concentration of formed during the process chloride ions (argentometric titration[2,3]) or of N-substituted p-nitrophenyl-β-aminovinylsulfones (UV spectrophotometring of the reaction mixture[3] over the range 330-340 nm, CF-4A spectrophotometer, quartz cells, ℓ = 10.0 mm).

the linear plot of $k_{obs.}$ vs. b. It should be noted that p--nitrophenyl-β-aminovinylsulfones formed during the reactions involving ammonia, primary and secondary amines influence the processes studied negligibly. Low reactivity of these compounds is due to effect of an unsaturated β-sulfovinyl group and its conjugating with amino group.

Comparison of the k values (Table 1) with each other shows that the structure of amine influences its reactivity in the processes studied strongly. Here both electronic and steric effects of a hydrocarbon radical are of great importance. For example, the transition from cyclohexylamine (No 10) to aniline (No 11) is accompanied by fall in the bimolecular reaction rate by 4 orders of magnitude due to changes in the inductive and resonance interactions of the corresponding radicals with amino group. But with the transition from diethylamine (No 13) to diisopropylamine (No 14) the process slows down approximately by a factor of 3000 though the basicities of these amines are essentially the same. This is caused exclusively by the increase in the steric screening of amino group in diisopropyl due to more bulky isopropyl groups.

It should be noted that the reactivity of tertiary amines studied does not differ from that of primary and secondary (with consideration of electronic and steric effects of their radicals). Thus it is possible to assume that the interaction mechanism of the amines studied all is completely identical and their reactivity could be described by a single correlation equation.

The most rigorously the steric and electronic effects of the structure of aliphatic amines can be calculated[5,8,9] by equation (3):

$$\lg k = \lg k_0 + \rho^* \Sigma\sigma^* + \delta E_N \qquad (3)$$

$\Sigma\sigma^*$ characterizes the inductive substituent effect at nitrogen atom, E_N is steric effect of the whole amine, ρ^* and δ denote sensitivity of the reaction series to the corresponding effect.

Table 1

Reaction Rate Constants of Amines with Trans-p-Nitrophenyl--β-Chlorovinylsulfone in Chlorobenzene at 25°.

NN	Amines	$k \cdot 10^3$ l/mol·sec	$k_b \cdot 10^3$ $l^2/mol^2 \cdot sec$	NN	Amines	$k \cdot 10^3$ l/mol·sec
1.	Ammonia	1.95 ± 1.31	103 ± 9	14.	Diisopropylamine	0.274 ± 0.009
2.	Methylamine	76.4 ± 3.3	4670 ± 310	15.	Methylpropylamine	3990 ± 30
3.	Ethylamine	48.2 ± 2.5	1340 ± 170	16.	Di-n-butylamine	875 ± 8
4.	Isopropylamine	12.3 ± 0.1	90.5 ± 0.9	17.	Di-n-amylamine	457 ± 4
5.	n-Butylamine	76.2 ± 0.5	643 ± 9	18.	Di-n-hexylamine	771 ± 9
6.	n-Hexylamine	65.4 ± 0.4	727 ± 11	19.	Dibenzylamine	13.3 ± 1.0
7.	n-Heptylamine	63.6 ± 0.1	961 ± 3	20.	Piperidine [3]	23600
8.	Allylamine	10.4 ± 0.9	164 ± 9	21.	Trimethylamine	21500 ± 1500
9.	Benzylamine	72.3 ± 1.0	513 ± 11	22.	Triethylamine [3]	24.2
10.	Cyclohexylamine	19.1 ± 0.4	104 ± 11	23.	Tribenzylamine	$(117 \pm 5) \cdot 10^{-5}$
11.	Aniline	$(251 \pm 5) \cdot 10^{-5}$	$(214 \pm 12) \cdot 10^4$	24.	N,N-Dimethyl-benzylamine	216 ± 5
12.	Dimethylamine	29100 ± 400		25.	Pyridine	1.09 ± 0.01
13.	Diethylamine	812 ± 8				

As one can see from the plot of $\lg k - \delta E_N$ vs. $\Sigma\sigma^*$ (see the Fig.) Eq.(3) can be successfully applied to the reaction studied and has the following form*):

$$\lg k = (4.00\pm0.31)-(4.78\pm0.29)\Sigma\sigma^*+(1.70\pm0.11)E_N \qquad (4)$$

(s=0.44; R=0.971; N=22)

The points for benzylamine (No 9) and dibenzylamine (No 19) deviate upwards markedly (more than by 1 log un.) from the correlation obtained. This is, probably, caused by the formation of IHB between benzene ring and hydrogen atom at a nitrogen atom of benzylamine fragment in the transition state[8]. It is interesting that with allylamine no IHB is formed. Therefore this amine has proved to be 7 times less active than benzylamine (cf. NoNo 8 and 9 in Table 1), though inductive effects of hydrogen radicals in them are essentially the same and steric screening of a nitrogen atom is even somewhat higher in the latter[5]. Due to these facts on determining the coefficients in Eq.(4) the points for benzylamine and dibenzylamine were not taken into account. The point for aniline (No 11) was also excluded, since it deviates downwards markedly (approximately by 1.5 order of magnitude) from the correlation obtained. In this case it occurs due to the conjugation effect between benzene ring and amino group, dedreasing the nucleophilic reactivity of the latter. Thus the conclusion can be drawn that the application of Eq.(3) for the combined treatment of the reactivity of aliphatic and aromatic amines provides a means for estimating the conjugation effect of α unsaturated group on the chemical activity of amino group.

It should be noted that the reactivity of pyridine (No 25) obeys the correlation obtained setisfactorily.

This indicates that the $\Sigma\sigma^*$ (1.50) and E_N(-0.24) val-

*) Values s, R, and N characterize mean-square deviation, correlation coefficient, and a number of points used for calculations, respectively.

ues[9] characterize satisfactorily electronic and steric effects of this amine structure, which is, apparently, of the same type that that of aliphatic α unsaturated amines in the reaction studied.

As to the dependence of catalytic activity of amines (k_b values in Table 1) on their structure, the results of treatment of the obtained data*) by Eq.(3) turned to be unsatisfactory: mean-square errors in the coefficients of equation are high enough and the correlation coefficient R=0.86. First of all this is due to the fact that k_b constants are complex values. They characterize the catalytic activity of amine in the reaction of the same amine.Therefore the amine structure effect is manifested here twice (as that of a reagent and of a catalyst) and hence each time we deal as if with a new reaction.

As said above, equation (4) describes the reactivity of the amines studied satisfactorily (Fig.1). With excluding tertiary amines from the consideration, the reactivity of primary and secondary amines (with the exception of benzylamine, dibenzylamine, and aniline) is described by the relationship:

$$\lg k = (4.60\pm0.43)-(5.52\pm0.43)\Sigma\sigma^{*}+(1.83\pm0.16)E_N \qquad (5)$$

(s=0.40; R=0.961; N=17)

The fact that coefficients in equations (4) and (5) coinside within the limits of errors confirms the idea about a single reaction mechanism of phenyl-β-halidevinylsulfones with amines of different classes. Since in the reactions of tertiary amines the formation of IHB is impossible (due to the absence of a hydrogen atom at nitrogen), the conclusion can be made that no IHB is also formed in the reaction involving primary and secondary amines. The latter is in good agreement with the conclusion about a single interaction mechanism of the substrate considered with dif-

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*)The point for aniline (No 11) was excluded from the consideration.

ferent amines[7] derived on the basis of studying solvent effect on the rate of the same reaction. Thus despite formal structural resemblance between β-halogenvinylketones and β-halidevinylsulfones their reaction mechanisms with amines are somewhat different. With interaction of β-halidevinylsulfone with primary and secondary amines the IHB in the intermediate (or in the close transition state) is absent, which is due to the lower ability of sulfogroup (over carbonyl) to form H-bonds[7,10].

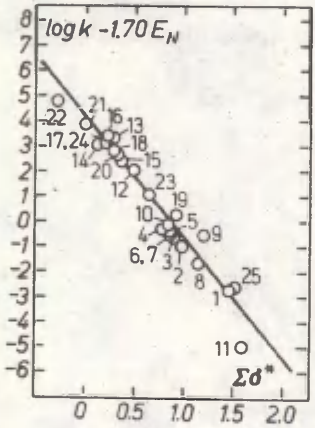

Fig.1. Comparison of the lgk - 1.70E_N values with $\Sigma\sigma^*$ for reactions of amines with trans-p-nitrophenyl-β-chlorovinylsulfone. For numbering of points see Table 1.

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Kinetic Study of Ionization of Nitroalkanes in Mixed Solvents. VI. Nitroethane in Water-Dimethyl Formamide and Water-Dimethyl Sulfoxide Mixtures

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The reaction rate constants of nitroethane and nitroethane-d_2 with hydroxide and m-chlorophenolate ions and aminoethanol are determined in water and in 50%(v/v) water-dimethyl formamide and water-dimethyl sulfoxide mixtures. Activation parameters of these reactions are calculated.

Some interesting regularities are found for ionization of nitroalkanes with transition from water to water - - DMF mixtures. Among them, first of all, the attention should be paid to a considerable decrease in the activation energy and increase in the absolute value of ρ^* with moderate increase in the ionization rate [1,2]. The increase in the rate itself must be ascribed [1] rather to the increase in the stability of the activated state than to the decrease in the stability of the initial one. Later on this conclusion was confirmed by the results of Cox and Gibson[3]. The decrease in the activation energy and increase in the absolute value of ρ^* were also interpreted [2] in terms of structural changes in the activated state. The activated state solvated by DMF was assumed to be so stable that even at moderate concentrations of DMF the reaction proceeded via this activated state despite the most part of the base was hydrated. Stabilizing influence of DMF increases with increase in the polarity of the activated state and results in the

growth of the absolute value of ρ^*.

The purpose of the present work was to more regorously verify the nature of solvation effects and to study the possibility of their "molecular" interpretation using the method of potential (or free) energy curves (see Ref. 4) formulated mathematically in the Marcus theory [5,6].

To accumulate the necessary experimental data the reaction of proton transfer was studied in both directions.

$$CH_3CH_2NO_2 + A^-(B) \underset{k_1^H}{\overset{k_1^H}{\rightleftharpoons}} CH_3CHNO_2^- + HA(BH^+)$$

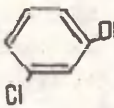
Since the medium properties influence not only the rate constant but also kinetic isotope effect [3,7], for some reactions the rates of deuteron transfer were measured

$$CH_3CD_2NO_2 + A^- \xrightarrow{-k^D} CH_3CDNO_2^- + HA$$

The following reagents were used in addition to those described elsewhere [2,8]:

$CH_3CD_2NO_2$ - synthesized as in [9,10], deuterium content is 96% (by density measurements and NMR spectra), b.p. 56.5 at 178 mm n_D^{20} 1.3919, d_4^{25} 1.0775;

$HOC_2H_4NH_2$ - rerectified, b.p. 114° at 90 mm, n_D^{20} 1.4539, d_4^{20} 1.0211;



- rectified, fraction with b.p. 103-104° at 12 mm, resublimed (60-70° at 5 mm, n_D^{40} 1.5565;

CH_3SOCH_3 (DMSO) - rectified, b.p. 93.0 - 93.5° at 20 mm, n_D^{20} 1.4772; d_4^{20} 1.1016.

In all experiments constant ion strenght of the solution (0.1) was maintained by adding NaCl.

The reactions involving hydroxyl ions were monitored by the stopped flow method, using the device constructed on the basis of attachment of Design Bureau of Biological Instrument Making of Ac.Sci. (USSR). Depending on the rate, the kinetic curves were registered by an oscillograph or an

automatic recorder. Working wave-lengths for nitroethane were 230 and 253-260 nm in water and in mixed solvents, respectively. The reactants were mixed on preparing the initial solutions (H_2O-DMSO) or in the mixer of the device (H_2O-DMF). In the latter case [2] the temperature was followed with the use of a thermistor built in the cell. Concentrations of the final solution were about $5 \cdot 10^{-4}$ mol/l on nitroethane and 0.05; 0.07; 0.10 mol/l on hydroxyl ion. The first order rate constants, k_m, calculated by the method of Rudakov [11], proved to be proportional to the alkali concentration. Mean values of the second order constants were obtained from the ratio $k_m / [OH^-]$. They are listed in Table 1.

The neutralization rate constant of $NCC_2H_4NO_2$, estimated elsewhere [2] by extrapolating the data for glycine buffer solution, was also determined by the flow method. Measurements were carried out in water at 25° on working wave-length 236 nm; the concentrations were about $2 \cdot 10^{-4}$ mol/l on nitroalkane, 0.10 and 0.05 mol/l on hydroxyl ion. The obtained value is 1340 ± 40 $l \cdot mol^{-1} \cdot sec^{-1}$ (45 runs).

Ionization induced by aminoethane was studied on a SF-4A spectrophotometer equipped with a photomultiplier and an automatic recorder, at 255 nm. Measurements were done in buffer solutions 0.1; 0.2; 1.0 (for nitroethane-d_2 0.1 and 1.0) at concentrations of aminoethanol from 0.01 to 0.10 mol/l.

M-chlorophenolate induced ionization was studied making use of an LP-60 polarograph on the electrode with forced drop separation. The drop in the limiting diffusion current at 1.2 and 1.4 V (for H_2O and H_2O-DMF, respectively) was followed against the saturated reference calomel electrode. Measurements were carried out for buffer ratios 0.01; 0.1; 1.0 at the concentrations of phenolate from 0.01 to 0.10 mol/l.

The bimolecular rate constants (Table 2) were calculated by the equations:

Table 1

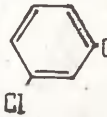
Reaction Rate Constants of Nitroethane with OH^- ($l \cdot mol^{-1} \cdot sec^{-1}$). Standard errors are given; n is a number of experiments.

Medium	^oC	k_1^H	n	$k_{-1}^H \cdot 10^7$	k^D	n
H_2O	11.0	-	-	-	0.208±0.002	14
	25.0	5.1±0.1	16	2.7 ± 0.7[a]	0.633±0.004	14
	35.0	-	-	-	1.54 ±0.03	8
H_2O-DMF	25.0	-	-	520 ± 70[b]	76± 3	11
	25.3	74 ± 7	26	-	-	-
	25.5	79 ± 3	14	-	-	-
	27.5	-	-	-	80± 2	12
	27.9	-	-	-	82± 3	7
	33.3	118±15	38	-	-	-
	37.3	-	-	-	110±12	10
	40.3	145±11	43	-	-	-
	45.0	-	-	740 ± 140[b]	-	-
	47.4	-	-	-	120±16	35
H_2O-DMSO	15.0	33±6	14		3.9±0.5	18
	25.0	68±6	38		7.0±1.3	53
	45.0	460±140	9		36±16	27

[a] from the values of k_1^H, pK_w, and pK_a of nitroethane[12];
[b] the value of $k_o/55.5$ for the buffer solution of m-chlorophenol.

Reaction Rate Constants of Nitroethane ($l \cdot mol^{-1} \cdot sec^{-1}$). Table 2

Standard deviations are given; n is a number of experiments.

Base	Medium	°C	$k_1^H \cdot 10^2$	$k_{-1}^H \cdot 10^2$	n	$k^D \cdot 10^3$	n
	H_2O	25.0 35.0	5.30±0.02 11.6 ±0.1	1.39±0.01 4.60±0.06	27 11	9.4±0.3	8
	H_2O-DMF	25.0 35.0	59.5 ±0.2 120 ±1.0	26.0 ±0.9 70 ±2	56 12	76±1	16
$HOC_2H_4NH_2$	H_2O	25.0 45.0	2.03±0.03 8.7 ±0.6	0.138±0.009 1.75±0.08	15 19	4.5±0.4	14
	H_2O-DMF	25.0 45.0	6.1 ±0.3 28 ±2	6.3 ± 0.5 48 ± 15	59 23		

$$(1 + \frac{1}{K})(k_o + k_1 [A^-]) = \mathfrak{K}$$

and

$$(1 + K)(k'_o + k_{-1} [HA]) = \mathfrak{K}$$

where $\mathfrak{K}$ is mobility, K is an equilibrium constant, k_o and k_1 are ionization rate constants, k'_o and k_{-1} are recombination rate constants, HA and A^- are acidic and basic components of a buffer solution. The R values were calculated by the literature data [12-14] or by the final depth of the reaction in kinetic measurements. Fig. 1 illustrates the plot of HK/(1+K) vs. concentration of m-chlorophenolate ion in the H_2O-DMF mixture where the K value is determined by the final depth of the reaction. Observance of a

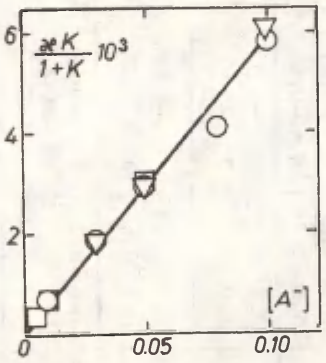


Fig. 1. Plot of HK/(1+K) vs. concentration of m-chlorophenolate ion in the H_2O-DMF mixture at 25° with the use of mean values of $\mathfrak{K}$. Buffer ratios are 1.0 (□), 0.1(0), and 0.01 (Δ).

Values of Activation Entropy (cal·mol^{-1}·degr.$^{-1}$) and Enthalpy (kcal·mol^{-1}) for Ionization (k_1^4 or k^D) and Recombination (k_{-1}^H) at 25°. Standard deviations are given.

Table 3

Reagents	Medium	Ionization		Recombination	
		$\Delta S_{\neq}$	$\Delta H_{\neq}$	$\Delta S_{\neq}$	$\Delta H_{\neq}$
$CH_3CH_2NO_2 + OH^-$	H_2O	-15	12,0 ± 0,4[a]	-10	23.3 ± 1,2[b]
	H_2O - DMF	-22	8.2 ± 0.5	-58	5,9 ± 4,4
	H_2O - DMSO	-2	14.2 ± 0.4		
$CH_3CD_2NO_2 + OH^-$	H_2O	-13	13.7 ± 0.6		
	H_2O - DMF	-39	3.2 ± 0,2		
	H_2O - DMSO	-3	13,5 ± 0,7		
$CH_3CH_2NO_2 + ClC_6H_4O^-$	H_2O	-18	13.7 ± 0.9	4	21,2 ± 0,3
	H_2O-DMF	-19	12,2 ± 1,6	-3	17,5 ± 0,8
$CH_3CH_2NO_2 + HOC_2H_4NH_2$	H_2O	-22	13,1 ± 0,7	7	23,3 ± 0,7
	H_2O - DMF	-18	13,8 ± 0,8	-2	18,5 ± 3,0

[a] by the literature data [15] for the range from 0 to 25°

[b] estimated by the temperature dependence of the k_1, pK_w, and pK values of nitroethane[12].

single linearity for all buffer ratios indicates the absence of a noticeable systematic error in the method used for determining K.

The k^D values (Table 2) were determined directly from the slope of the dependense of α on the concentration of basic component of a buffer solution for the lowest buffer ratio where the reaction was practically irreversible. Thus the k^D value of aminoethanol was obtained from the data for buffer ratio 0.1, and the k^D value of m-chlorophenolate was determined from the data for ratio 0.01. The rest of the data were used just as criterion of the limits of the slope observed.

Activation parameters of the reaction (Table 3) were calculated from the primary (not averaged) values of the bimolecular rate constants. For example, for the reaction of $CH_3CH_2NO_2 + OH^-$ in the H_2O-DMF mixture not only 4 values given in Table 1, but all 121 values of the bimolecular constants were used. Since at the given temperature interval the accuracy of determining activation parameters depends, first of all, on the accuracy of determining rate constants, the values obtained by this method and their errors should not differ significantly from the true ones.

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Kinetic Study of Ionization of Nitroalkanes in Mixed Solvents. VII Verification of Applicability of the Marcus Theory

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Basic equations of the Marcus theory describing the kinetic isotope effect as a function of the equilibrium constant and deviations from the linearity in the Brønsted coordinates are discussed. The kinetic isotope effect in the ionization reaction of nitroethane is shown to be little dependent on the equilibrium constant and determined, mainly, by some factors not taken into account by the Marcus theory. As to the curvature in the Brønsted plot it is due to the differences in the solvation rather than to the ΔpK of acid-base pairs involved in the proton-transfer reaction.

The Marcus proton transfer theory [1,2] is, by intention, the basis for interpreting experimental rates of proton transfer. It is called for the quantitative description of two main, according to Bell,[3] regularities characteristic of the transfer reaction: curvature in the Brønsted plot and the maximum of kinetic isotope effect at zero free energy of the reaction. The basic equation of the theory can be derived in terms of the model of the crossing of potential energy curves. Thus the corresponding parameters are given quite definite physical meaning to. Here, however, the realization of some conditions is necessary.

1) coincidence of the profiles of free and potential activation energy, 2) constancy of force constant, and 3) constancy of transfer distance. The realization of the first condition is not apparent[5]. It is even doubtful for the second and third conditions[4].

According to the Marcus theory [1,6] the relatively simple relationship

$$\Delta F^* = \frac{\lambda}{4}\left(1 + \frac{\Delta F_R^{0'}}{\lambda}\right)^2 \qquad (1)$$

between the observed activation free energy (ΔF^*) and the reaction free energy ($\Delta F_R^{0'}$) is valid for the reaction inside the so called reaction complex (reaction 2b). To describe the plot of ΔF^* vs. $\Delta F^{0'}$ (the observed free energy of the reaction) of the over-all process two constants (W_r and W_p)

$$RH + A^- \overset{W_r}{\rightleftharpoons} RH \cdot A^- \qquad (2)$$

$$RH \cdot A^- \overset{\Delta F_R^{0'}}{\rightleftharpoons} R^- \cdot HA \qquad (2b)$$

$$R^-HA \overset{W_p}{\rightleftharpoons} R^- + HA \qquad (2c)$$

referring to the steps of the reaction complex formation are introduced. Hence,

$$\Delta F^{0'} = W_r + \Delta F_R^{0'} - W_p$$

and accepting* the assumption about separability of the solvent reorganization and proton transfer effects, the observed activation free energy is calculated[1] by the equation

$$\Delta F^* = W_r + \frac{\lambda}{4}\left(1 + \frac{\Delta F^{0'} - W_r + W_p}{\lambda}\right)^2 \qquad (3)$$

The values of the W_r, W_p, and λ parameters can be determined from Eq.(3) only. Hence, the possibility to describe the curvature in the Brønsted plot with this equation is not a verification of the Marcus' model.

*This assumption is valid for the case of asynchronous transfer[7] but is hardly a general rule.

Therefore one can agree with the opinion [8] that the basic equation of the Marcus theory is of no strict theoretical background and is empirical.

The purpose of the present work is to check the possibility to interprete the obtained kinetic data on the ionization of nitroethane [9] within the framework of the Marcus theory. The experimental check of the theory discussed is possible owing to the presence of the data on the kinetic isotope effect. The equation for describing the latter can be [10] presented in the form

$$\Delta F^*_D - \Delta F^*_H = \frac{1}{4}(\lambda_D - \lambda_H) + \frac{1}{4}(\Delta F^{0'} - W_r + W_p)^2\left(\frac{1}{\lambda_H} - \frac{1}{\lambda_D}\right) \quad (4)$$

where subscripts H and D refer to proton and deuteron, respectively. Though Marcus himself suggests another form of the equation, in both cases, provided that $W_p - W_r$ = const, the observance of a bell-shaped plot between the values of the logarithms of kinetic isotope effect and the equilibrium constant of reaction (2) with the maximum in the region $\Delta F^{0'}$ - const = 0 is necessary. With the structure of nitroalkane being constant and only that of the base changing, the supporters of the Marcus formalism feel no doubts that condition $W_p - W_r$ = const will be realized [10-12].

Table I summarizes values of the equilibrium constants and kinetic isotope effect of the ionization of nitroethane calculated from the data of our preliminary communication [9]. These data referring to the region $\lg K \approx 0$ together with the literature data [13,14] for the regions $\lg K > 0$ and $\lg K < 0$ lead to the result illustrated in Fig. 1. The absence of a single dependence in the logarithmic coordinates of kinetic isotope effect and equilibrium constant indicates that the ratio k^H/k^D cannot be a function of reaction free energy only. As a matter of fact, practical absence of the dependence between the values of $\lg(k^H/k^D)$ and ΔpK_a for the ionization reaction of arylnitroethanes [15] indicates the same.

Table 1

Values of Equilibrium Constants ($K=k_1^H/k_{-1}^H$) and Kinetic Isotope Effect (k_1^H/k^D) of Ionization of Nitroethane at 25°.

Mean errors are given.

Base	Medium	K	k_1^H/k^D
OH^-	H_2O	$(1.9\pm0.2)\ 10^7$	$8,1\pm0,2$
	H_2O - DMF	$(1.5\pm0.1)\ 10^6$	$1.0\pm0,1$
	H_2O - DMSO	$8 \cdot 10^{8a}$	$9.7\pm2,0$
$ClC_6H_4O^-$	H_2O	$3.8\pm0,1$	$5.6\pm0,2$
	H_2O - DMF	$2,3\pm0,1$	$7.8\pm0,1$
$HOC_2H_4NH_2$	H_2O	15 ± 1	4.5 ± 0.4

Thus with the ionization reaction of nitroalkanes as an example an unambiguous conclusion can be drawn that equation (4) resulting from the major postulates of the Marcus theory is invalid.

It may be possible, of course, that the W_p-W_r value depends strongly on the base or solvent. In this case, however, the theory cannot be verified and thus it is deprived of any sense. Therefore the conclusion about inability of the Marcus theory to describe the kinetic isotope effect of the ionization of nitroakanes is even independent of the condition W_p-W_r=const. Thus both Eq.(3) and any other postulate of the Marcus theory cannot be applied to the given reaction.

On the other hand, the opinion exists [16,17] that the curvature in the Brønsted plot has little in common with the degree of the proton transfer and reflects differences in the solvation of a catalyst. It has been shown [16,18] that

[a] Estimated by the data from Ref. 13.

the rate of proton transfer from carbon acids RH to bases A^- can be described by a single dependence which assumes constancy of the slope in the logarithmic form of the Brønsted equation (β) for the whole range $5.8 \leq pK_{RH} \leq 20$ and $-1.8 \leq pK_{AH} \leq 15.8$ Though the correlation error exceeds obviously the experimental one, it indicates that [16]

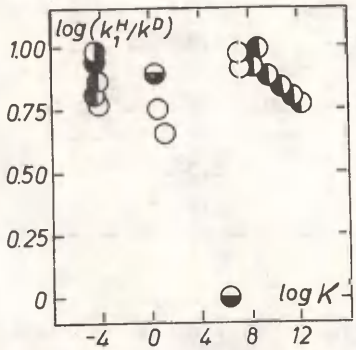

Fig. 1. Kinetic isotope effect (k_1^H/k^D) vs. equilibrium constant ($K = k_1^H/k_{-1}^H$) of ionization of nitroethane in water (○) and in mixtures: water - DMSO (◐), water- DMF (◒), water--acetonitrile (●), water-trifluoroethanol (◑).

dependence of β constant on pK_{AH} is almost completely determined by base properties. Even in such an utmost case when ionization reactions of phenylnitroethane (pK_a = 6.8) and acetone (pK_a is about 20) are compared (the pK_{RH} values differ by 13 un.), the ionization rate depends on the base in the same manner (see Fig.2). In other words, the β value is not a function of the $pK_{RH} - pK_{AH}$ value as required by the Marcus theory. Hence, the curvature in the Brønsted plot is not accounted for by changes in the activation free energy inside the reaction complex and equation of type (3) is deprived of the content given to it by this theory.

Thus the conclusion rises that the Marcus theory cannot be applied to the ionization reaction of nitroalkanes. The

property $\beta \neq$ const. itself, for whose description this theory is constructed (for the proton transfer in non-diffusion region) is illusory.

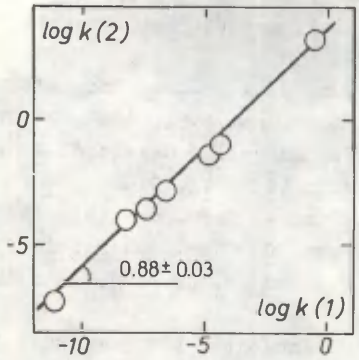

Fig. 2. Relationship between lgk values [19] of ionization of phenylnitromethane (2) and acetone (1) induced by water, amines, carboxylate, and hydroxylic ions.

Thus the conclusion [20] about quasitheoretical nature of the Marcus proton transfer theory is confirmed.

Acknowledgement

We are greatly indebted to prof. V. Palm for valuable discussions of the main conclusions of this communication.

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Kinetic Study of Ionization of Nitroalkanes in Mixed Solvents. VIII Effect of Aprotic Dipolar Component

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Results of studying ionization reactions of nitroethane and nitroethane-d_2 in water-dimethylformamide and water-dimethylsulfoxide mixtures are discussed. The accelerating effect of aprotic component is shown to be due to the stabilization of the activated state, the effect increasing with increase in the polarity of the latter. Isokinetic (compensation) relationship with some deviations is found. Possible causes of these deviations are discussed. Activation parameters of the kinetic isotope effect of the nitroethane reaction with hydroxyl ion in water-DMF mixture do not agree with the current theories which practically neglect the character of solvent-solute interactions.

The data obtained for the reaction

$$CH_3CH_2NO_2 + A^-(B) \rightleftharpoons CH_3CHNO_2^- + HA(BH^+)$$

in water and in mixed solvent H_2O - DMF indicate that for all bases studied the addition of DMF accelerates both direct and reverse reactions. Though according to Parker[2] the solvation of nucleophile is usually considered to be a decisive factor, up to present thoroughly studied reactions of nucleophilic substitution [3-5] are known where solvation

of the activated state is of the most importance. Therefore the suggestion which does not reduce the effect of aprotic solvent to desolvation of nucleophile only is a rule rather than an exception.

To describe the effect of a primary solvent shell of the activated state in the reaction of carbon acid RH with a base, B, the scheme [6] involving the resolvation of a base by an organic solvent, S, is suggested:

$$\begin{array}{ccc} B \cdot H_2O & + S \underset{}{\overset{K}{\rightleftharpoons}} & B \cdot S + H_2O \\ +RH \downarrow k_1 & & +RH \downarrow k_2 \\ A_1^{\neq} & & A_2^{\neq} \end{array} \qquad (1)$$

where RH is nitroalkane and $A_1^{\neq}$ and $A_2^{\neq}$ are activated states. The observed rate constant of such parallel reactions is expressed by the equation:

$$k = k_1\left(1 - \frac{K}{K + \frac{[H_2O]}{[S]}}\right) + k_2 \frac{K}{K + \frac{[H_2O]}{[S]}} \qquad (2)$$

Though in the range $0.05 \leq N_S \leq 0.30$ real deviations (due to effect of the secondary solvation) were found, equation (2) describes the dependence of the observed rate constant on N_S for water-DMF and water-acetonitrile [6] mixtures satisfactorily.

Causes of the higher stability of the activated state solvated by DMF are not quite clear. The effect depends considerably on the reactivity of an acid-base pair involved in the reaction, it being quite possible that the value of the stabilizing effect of DMF and polarity of the activated state change into the same direction [6,7]. The purpose of this work is to study in detail the structure of the activated state and to verify this assumption.

Since we were forced to give the Marcus theory [8] up, the main source of information about the structure of the activated state was in studying the values of the cross-terms

in the correlation equation proportional to the products of substituent constants. Since the substituents are situated in nucleophile and electrophile, the values referring just to the activated state are meant. One should keep in mind that due to the rough approximation neglecting the"interaction of groups" in the activated state[9] the ionization rate of carbon acids is almost always dependent on a number of substituent parameters, i.e. the interaction of substituents with the reaction center occurs via different types of interaction. The "interaction of groups", i.e. cross substituent effects in the reaction components, also proceed by some concrete types of interaction and should be ascribed to the corresponding structural factors rather than to the pK_{AH} (or pK_{RH}) values.

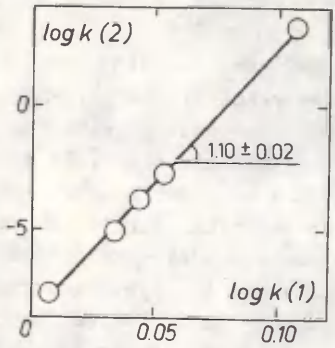


Fig. 1. Relationship between the lgk values [1,7] of the ionization of 2-cyano-I-nitroetnane (2) and nitroethane (I) induced by water, carboxylate and hydroxyl ions.

Fig. 1. illustrates the relationship between the lgk values of the ionization of two nitroalkanee, nitroethane, and 2-cyano-I-nitroethane. In good approximation they differ in the intensity of inductive interaction only. The slope

of the plot, exceeding unity with certainty indicates that the contribution of the inductive stabilization of the activated state increases somewhat with increase in the reaction rate. An analogous relationship is also observed for I-arylnitroethanes: lgk for m-methyl- and m,m' - dinitrosubstituted compounds increases from 1.0 for morpholine to 1.8 for hydroxyl [10]. Thus in both cases the increase in basicity (hardness) of a donor is due to the increase in the "carbanionicity" and, hence, in the relative weight of electrostatic stabilization of the activated state. Being formulated in this way the result is quite in agreement with common rules of acid-base interaction[11].

At low values of N_{DMF} in the water-DMF system the quasi-elementary reaction proceeding through the activated state $A_2^{\neq}$ (see scheme 1) can be characterized [7] by the value

$$k - k_1 = \Delta k$$

The effect of the DMF addition (Δk) increases with the increase in the system reactivity (k_1). Fig. 2.represents the corresponding dependence together with the data of the present study in the logarithmic scale. If for the $CH_3CH_2NO_2$+ + Cl_2CHCOO^- system the addition of DMF leads to two-fold acceleration of the reaction, for the $CH_3CH_2NO_2$ + OH^- system the reaction rate increases by a factor of 14. Thus, in accordance with the above parallel behavior of the value of the addition effect and reactivity can be considered as parallel changes in polarity of the activated state and the value of the addition stabilizing effect.

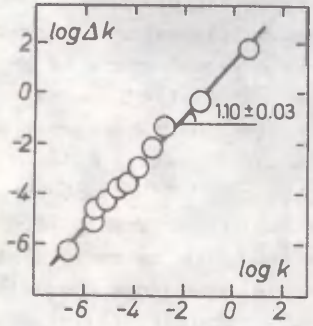
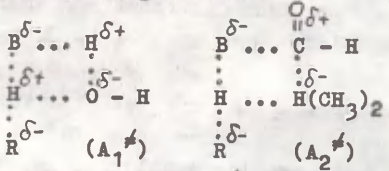


Fig.2. Plot of $\lg \Delta k$ vs.$\lg k_1$ for the reactions of nitroethane, 1.3- dinitropropane, and 2-cyan-1-nitroethane with oxyanions in the water-DMF system. N_{DMF} = 0.189.

The activated states $A_1^{\neq}$ and $A_2^{\neq}$ solvated in the first shell by water and DMF, respectively, can be probably expressed by the following schemes:



Higher stability of the state $A_2^{\neq}$ is accounted for both by higher basicity and polarizability of DMF. There are not enough available data to solve the problem about relative weights of the two factors experimentally. However, on the basis of the non-conjugated proton transfer model [12] the

polarizability should be expected to be more significant.

Values of energy characteristics of the proton transfer reaction are summarized in Table 3 of Ref. 1. On the example of the reaction of $CH_3CH_2NO_2 + OH^-$ in pure water and in the water-DMSO system one can distinctly see that the assumption [13,14] about enthalpic nature of aprotic solvent effects does not held. This result seems to be quite a reasonable consequence of scheme (I) itself.

When analyzing the activation parameters, we proceeded from the assumption that the linearity between the free energy and enthalpy values could [15] be interpreted in terms of isokinetic (compensation) relationship. From Fig. 3 one can see that with transition from water to mixtures with an aprotic dipolar solvent the dependence characteristic of pure water is, in general, retained. Deviations are observed for the reactions of $CH_3CD_2NO_2 + OH^-$ in H_2O-DMF and for $CH_3CH_2NO_2 + OH^-$ in H_2O - DMSO.

Isokinetic relationship for reactions in solvents is believed [17-19] to require not only constancy of a reaction mechanism but also constancy of the type of solvation interactions. As to the similarity of pure water with its mixtures with DMF and acetonitrile, these aprotic solvents are known to insignificantly break the hydrogen bond system in pure water[19-21]. It is quite possible that additions of DMF even increase somewhat structurization of water. Thus separation of the rate of proton spin-lattice relaxation in the H_2O-DMF)-d_7 system into contributions of free and solvent--soivent bond(associates with DMF) water molecules indicates that the relative relaxation rate of protons of free molecules increases over that in pure water[22]. There is a discrepancy between the opinions about DMSO (see, for example, Refs. 23,24), though the conclusion about the character of interaction between water and DMSO as associative (breaking the structure of water) seems to be more reasoned. If, according to Blandamer[19], DMSO is considered to

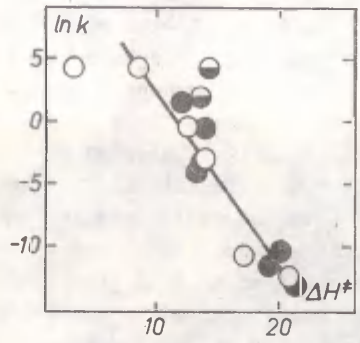


Fig. 3. Isokinetic relationship for the ionization of nitroethane in water (●), mixed solvents: water-DMF and water-acetonitrile (○), and in the water-DMSO system (◒) at 25° (acc. to Refs. 1,6,16).

destroy the structure of water, the deviation of the point for the reaction of $CH_3CH_2NO_2 + OH^-$ in the H_2O -DMSO mixture would be clear.

According to the literature data [14], aprotic solvents differentiate hard and soft anions enthalpically mainly. The differentiating effect of DMF exceeds that for DMSO due to somewhat higher molecular polarizability of DMF. Thus in terms of the commonly used physical picture of aprotic solvent effects [2,25,26] the reactions of nucleophilic substitution may be expected to have higher activation enthalpies in DMSO. In the mixtures with water the solvent structure effect is also present, the decrease in the structurization of water increasing, probably, the relative entropy of the softer (less hydrated) state. This would correspond to the deviation from the general isokinetic dependence for the data of the H_2O-DMSO mixture just to the direction of more positive activation entropies.

Deviation of the point for $CH_3CD_2NO_2 + OH^-$ in the H_2O -

-DMF mixture cannot be accounted for by solvation differences. It can occur due to changes in the proton transfer mechanism only. According to the classical theory of kinetic isotope effect suggested by Westheimer [27] the value of the effect is determined, mainly, by a difference in zero-point energies of the initial state and symmetry of the activated state [28]. On this basis Bell has suggested the condition for classical isotope effect for ionization of carbon acids $0 \leq E^D - E^H \leq 1.2 kcal.mol^{-1}$, the higher values should indicate the tunneling of a light isotope[29]. Activation parameters of the isotope effect obtained in this work (Table 3 in Ref. 1) deviate into opposite direction corresponding, according to the same logic, to the better tunneling of a heavy isotope. Though with smooth repulsion potentials the quantum-chemical transfer theory [30] assumes the possibility of the better tunneling, in this case its realization should require enormous changes in the force constants with transition from pure water to its mixture with DMF. Thus the result obtained is at variance with existing theories of kinetic isotope effect. This indicates that they neglect actually the specific character of the condenced phase.

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ON SOME PECULIARITIES OF ISOPARAMETRIC RELATIONSHIPS IN THE GROUP OF TRIARYLCARBOCATIONS

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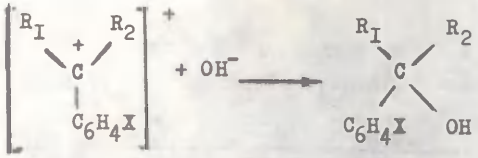
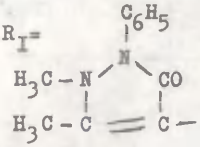
The results of kinetic study of the interaction of p-dimethylamino,p'-methoxytriphenylmethylcation derivatives with hydroxide ion in aqueous solution are compared with those for analogous reaction series studied elsewhere.The role of the relationship of electronic and solvation effects as a determining factor of the reactivity control type of conjugated carbocations is discussed.

In the previous works dealing with the kinetic study of the carbinol formation process in the series of triarylcarbocations of mono[1]- and diantipyrine[2] groups as well as in the Malachite Green derivatives[3,4] and their analogues with a p-$H(CH_3)_2$ group[5,6](series I,II,III,and IV,respectively) it has been showed that the isokinetic relationship[7,8] type and the reactivity control type were dependent on the length of the conjugation chain. While in the series of carbo-



I: R_I=  =A; R_2= p-$(CH_3)_2$NPh ;

II: R_I=R_2=A ;
III: R_I=R_2= p-$(CH_3)_2$NPh;
IV : R_I= p-$(CH_3)_2$NPh; R_2= Ph.

cations with rather developed conjugation chain (I,III) one can observe the enthalpy control of reactivity,in the series having the shortened chain of conjugation (II,IV) the entropy control is in action. Quite natural explanation of this phenomenon can be obtained by assuming that the value of the δ^+-charge of the carbonium center is responsible for its electrostatic solvation and, as a result, for the entropy of the initial state of the reacting system.[1,6-8] Thus,for a reaction series of intermediate character one could expect the change in the reactivity control type even with the relatively narrow interval of the δ^+-charge variation, for example, variation in the substituent.

In order to check this assumption the kinetics of formation of a number of p-dimethylamino,p'-methoxytriphenylcarbinol derivatives in aqeous solution has been studied at the temperature interval 15 - 50°C.[9,10] Some of the kinetics and correlation analysis results obtained are given in Table 1.

Table I.

Kinetics and Correlation Parameters for the Formation of p-Dimethylamino,p'-Methoxytriphenylcarbinol Derivatives in Water

X	k_{25°	E $\frac{\text{Kcal}}{\text{mol}}$	IgA	$\frac{\delta \Delta H^{\neq}}{\delta \sigma}$	$\frac{\delta \Delta S^{\neq}}{\delta \sigma}$	ρ_{25°
p-Me	I2.0	I2.6	I0.29	-9	-22	$\pm$ 0.96 0.03
m-Me	I3.6	I2.2	I0.09	-I0	-28	
p-OMe [I4]	I3.2	-	-	-	-	
H	I5.9	II.5	9.67	-	-	
m-OMe	I7.5	II.9	I0.00	+5	+I7	$\pm$ 0.37 0.03
p-Br	20.7	I2.3	I0.36	+3	+I2	
m-Br	22.2	I2.9	I0.79	+4	+I4	
m-HO_2	38.9	I2.2	I0.56	+I	+6	-

In agreement with the above assumptions, two separate isokinetic relationships have been found to exist in the reaction series under consideration.While the electron-repelling substituted carbocations show the isokinetic relationship with the enthalpy control (β = 358 K),those containing electron-withdrawing substituents appear to be entropy-controlled (β= 259 K) In accordance with this the angular Hammett plot has a break of linearity at X=H (see Fig.1).

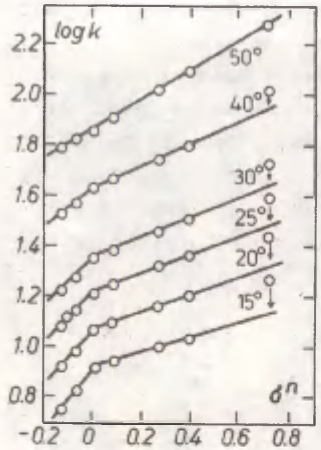


Fig.I. The substituent effects on the rate constants of the formation of p-dimethylamino,p'-methoxytriphenylcarbinol derivatives. The numbers are: I.p-CH_3 2.m-CH_3 3.p-OCH_3 I4 4.H 5.m-OCH_3 6.p-Br 7.m-Br 8.m-NO_2

All these results are consistent with the above considerations.

Thus,it may be concluded that in the series of carbocations under consideration the σ^+-charge value of the carbonium center is quite close to the "critical" value of this parameter. As soon as this value is being achieved,for example,by means of electron-withdrawing substituents,the formation of the second solvation sphere of the carbonium center occurs[11,12], the entropy becoming the prevailing factor of reactivity.

It is noteworthy that the above explanation is essentially identical to that given earlier when interpreting the phenomenon observed with "transition" of the isokinetic temperature in the Malachite Green series[16], [17].In the latter case the thermal destroying of the water structure has been supposed to be responsible for

increasing the solvation of carbocations (with entropy as the governing factor of reactivity).

Thus,in the conjugated carbonium series the entropy control is favored both by temperature and the charge localization on the central carbon atom.

Retention of the only reactivity control type for the majority of the carbocation series studied earlier finds its explanation in the fact that the $\delta+$ -charge value in these series differs significantly from the "critical" value of this parameter and therefore cannot be reached by means of such a weak factor as the substituent effect.

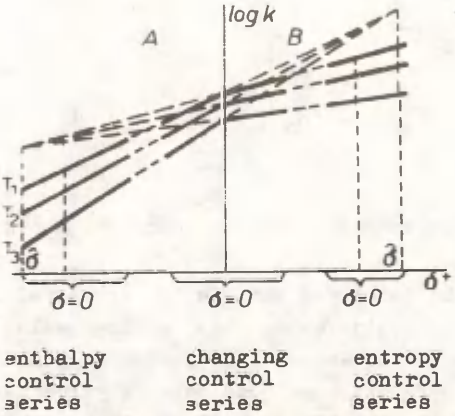


Fig.2. The influence of the charge distribution on the reactivity control type for the conjugated carbonium ions.

A - enthalpy control region

$$\frac{\partial_\sigma H^{\neq}}{\partial\sigma} < 0;\ \frac{\partial_\sigma S^{\neq}}{\partial\sigma} < 0;\ \frac{\partial_\sigma \theta^{\neq}}{\partial\sigma} < 0;\ \rho > 0;\ (\beta > \bar{T}_{exp})$$

B - entropy control region

$$\frac{\partial_\sigma H^{\neq}}{\partial\sigma} > 0;\ \frac{\partial_\sigma S^{\neq}}{\partial\sigma} > 0,\ \frac{\partial_\sigma \theta^{\neq}}{\partial\sigma} < 0;\ \rho > 0;\ (\beta < \bar{T}_{exp})$$

An arbitrary scale (Fig.2) illustrates the above considerations. From this figure it can be immediately concluded that it is impossible to reach the isoparametric value of the eubetituent constant ($\hat{\sigma}^{13}$), because the inversion of the control type will occur before the point of independence of the rate constants on temperature has been reached. For example, the $\hat{\sigma}$-value for the Malachite Green series is supposed to be equal to 3.07. However, it is quite evident that on attempts to have such a eubetituent effect in this reaction series we shall obtain the new series with the entropy control and with the $\hat{\sigma}$-value shifted far to the negative region of the eubetituent constants (as it is in the p-dimethylamino, p-methoxytriphenylcarbocation series[6]), and vice verca - See Table 2.

Table 2.
Isoparametric Values of the Substituent Constants for the Formation Reaction of Triarylcarbinols in Water.

Series	β	Dominating parameter	$\hat{\sigma}$
I	360	$H^{\#}$	+3.78
II	230	$S^{\#}$	-2.59
III	333	$H^{\#}$	+3.07
IV	250	$S^{\#}$	-2.23

It may be concluded that in contrast to the isokinetic temperature, having in some reaction series the real physical meaning[16,17], the isoparametric relationship with the $\hat{\sigma}$-values seems to be quite formal. It should be emphasized that irrespectively of the

peculiarities of the isoparametric relationships observed, both substituent effect ($-\frac{\delta \Delta G^{\#}}{\delta \sigma}$) and the reaction constants ($\rho = -\frac{1}{2.3RT} \cdot \frac{\delta \Delta G^{\#}}{\delta \sigma}$) keep their sign in all carbocation reactions series studied up to the present moment[1-6,9,10,15-17]. Such a result has a strong support from a simple electrostatic interpretation of the interaction of the opposite charges.

It is noteworthy that the increase in temperature causes the decrease in the slope of the Hammett plot, and at 50°C a single linear dependence for both electron-repelling and electron-withdrawing substitited carbocations is held:

$$\lg k = (1.859 \pm 0.002) + (0.588 \pm 0.006)\sigma^{n} \; ;$$

r 0.9997; n 7; s 0.001 ; See also Fig.1.

Thus, the neccessity of investigation of the problem "structure - reactivity" at more than one temperature[8,18] has been confirmed.

Experimental

The kinetic investigation of the discussed reaction was carried out as described in[10].

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NUCLEOPHILIC CONSTANT OF ORTHO-FLUORINE AND NUCLEOPHILIC CONSTANTS OF FLUORINE GROUPS σ^-_{3F}, σ^-_{4F}, σ^-_{5F} IN BENZENE RING. THE ELECTRONIC WITHDRAWING EFFECT OF FLUORINE GROUPS FROM 2,3,4 ATOMS OF FLUORINE UPON THE ORIENTATION OF NUCLEOPHILE IN POLYFLUOROBENZENES

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From the data on reaction kinetics of isomeric tetra-, penta-, and hexa- fluorobenzenes with sodium methoxide in methanol nucleophilic constants of fluorine groups in benzene ring were calculated: for 3 atoms of F(1,3,4)* σ^-_{3F}=0,83; for 3 atoms of F(2,3,5) σ^-_{3F}=0.89; for 4 atoms of F (2,3,5,6) σ^-_{4F}=1.06; for 5 atoms of F(2,3,4,5,6) σ^-_{5F}=1.14; as well as nucleophilic constant of ortho-fluorine in these compounds was estimated : σ^-_{o-F}=0.21±0.03.

The direction of substitution of nucleophile for fluorine in i-tetrafluorobenzenes and pentafluorobenzene coincides with that of maximum electrono-withdrawing effect of the remaining fluorine atoms in polyfluorobenzene and can be determined by the calculation from Hammett equation with the use of nucleophilic constants of fluorine groups.

Many studies are devoted to the determination of σ^-_{o-F} value, information on them is summarized in the review articles of M. Charton,[1,2] S.M. Shein et al.[3], D.A. Jones and G.G. Smith,[4] in the monographs by Y.A. Zhdanov, V.I. Minkin,[5] V.A. Palm[6]. A great number of investigations on the

* The position of fluorine atoms in benzene ring is indicated

determining σ_o of various substituents, including fluorine, were made by V.M. Maremäe-(Nummert) et.al.[7-12]

σ_{o-F} value varies within the large range 0.13-0.93 and depends considerably on the reaction series type [1-12]. The variety of σ_{o-F} is not accidental, it isn't the error of experiment, but it is a consequence of ortho-effect that is changed with the transition from one substrate to another, from one reaction series to another. Mathematical ways for the estimation of ortho-effect contribution to the σ_o value of substituent isn't developed for the present.

To obtain σ_{o-F} as purified from the influence of ortho--effect as possible the reaction series with removed reaction center are usually chosen, e.g. reactions of phenylpropiolic acids[13]. The average value of σ_{o-F} calculated from these series is 0.29 [3].

In the light of the said above, working at the programme on reactivity prediction of polyfluorobenzenes with the general formula $C_6F_nH_{6-n}$, we did not put the task to obtain a single value of σ_{o-F} suitable for all types of reaction series.

As an object of the present study we set the task of determination of σ^-_{o-F} value that is realized, in fact, in one of the reaction series of aromatic nucleophilic substitution, e.g., in the reactions of polyfluorobenzenes with the general formula $C_6F_nH_{6-n}$ (where n=1÷ 6) with sodium methoxide. It should be noted that the reactivity of polyfluorobenzenes in the nucleophilic substitution reactions correlates satisfactorily, while using the average value of σ^-_{o-Cl} =0.3[3] in the limits of Hammett equation, the average value of σ_{o-Cl} from the reactions of phenylpropiolic acids is slightly lower and equals 0.25[3,13].

For the determination of σ^-_{o-F} we used the data on the reaction kinetics of the isomeric tetrafluorobenzenes [14] pentafluoro- and hexafluoro- benzenes[15-17] with sodium methoxide in methanol, Hammett equation as a calculating formula $\lg k/k_o = \rho\sigma^-$, where "k" is a rate constant of polyfluoro-

benzene reaction from the series of $C_6F_nH_{6-n}$ with sodium methoxide in methanol at 50°C (kinetics of i-tetrafluorobenzene reactions with sodium methoxide being measured at 50° only[14]; k_o is a rate constant of the reaction of unsubstituted fluorobenzene with sodium methoxide, i.e. C_6H_5F, lgk_o is an initial point of the correlation equation; ρ is a reaction constant characterizing relative sensivity of the given reaction conversion:

$$C_6F_nH_{6-n} + CH_3ONa \rightarrow C_6F_{n-1}H_{6-n}OCH_3 + NaF$$

to the succesive accumulation of fluorine in benzene ring with the transition from C_6H_5F to C_6F_6; σ^- is a nucleophilic constant of substituent group, i.e., a constant summing up the influence of the electronic effect of fluorine atoms in the molecule of polyfluorobenzene upon the reaction center and characterizing reactivity of substituted fluorine. The value of σ^-_{o-F} can be determined from nucleophilic constants of the groups from 3,4, and 5 atoms of fluorine, if assuming the additivity of a separate fluorine atom electronic effects in the influence on the reaction center at their successive accumulation in benzene ring. There are reasons for this assumption: additivity of fluorine atom electronic effects on such property as pK_a of fluorobenzoic acids is shown in the studies of R. Filler et al., [18] V.A. Koptyug et al.[19]. Provided that additivity of fluorine atom electronic effects in the influence on the compounds of series $C_6F_nH_{6-n}$ with sodium methoxide is realized it can be written for nucleophilic constants of fluorine atom groups : for 5 atoms of fluorine in hexafluorobenzene (2,3,4,5,6) $\sigma^-_{5F} = 2\sigma^-_o + 2\sigma_m + \sigma^-_p$; for 4 atoms of fluorine (1,2,4,5) in pentafluorobenzene, where methoxide group is substituted mainly for the 3rd fluorine atom in para-position to H[15,17] $\sigma^-_{4F} = 2\sigma^-_o + 2\sigma_m$; for 3 fluorine atoms in 1,2,3,4-tetrafluorobenzene, where methoxide is substituted for the 2nd (4th) fluorine atom (1,3,4)[20] $\sigma^-_{3F} = 2\sigma_o + \sigma_m$; for 3 atoms of fluorine (2,3,5) in 1,2,3.5-tetrafluorobenzene, where the 1st (3rd) fluorine atom is replaced by methoxide group [20] $\sigma^-_{3F} = 2\sigma_m + \sigma^-_o$

and so on (see Table 1). Generally used values 0,062 and 0,337 are taken for σ^-_p and σ_m, respectively [21]. The value of reaction constant can be defined if we neglect ortho-effect of 2 fluorine atoms and consider the compounds of series $C_6F_nH_{6-n}$ as a part of reaction series: (m,- p-) $RC_6H_4F + CH_3ONa$ (CH_3OH). Naturally, this solution is approximate and causes certain mistake in the final result. As shown by calculation this mistake, expressed in the terms of σ, is relatively low and equals ± 14%, but expressed in the terms of "k" reaction rate it is considerably higher. However, at present in the absence of more accurate ways of solution of this problem this approximate solution allows to obtain practically valuable results on reactivity prediction. Calculated from the data of Ref. 22 value of ρ is 7.1552; close value of ρ=7,0 is obtained in Ref. 23. Substituting the lgk values of polyfluorobenzene reactions and lgk_o of fluorobenzene with sodium methoxide and then reaction constant ρ = 7,1552 into the Hammett equation, we determine the values for nucleophilic constants of fluorine atom groups in benzene ring: for 5 atoms of fluorine (2,3,4,5,6) σ^-_{5F}= 1.14 (see Table 1,2). In Ref. 24 the obtained value for σ^-_{5F} is lower by 0.164 sigm un., since the higher value of ρ=7.55 was used. For 4 atoms of fluorine (1,2,4,5) σ^-_{4F}=1.06; for 3 atoms of fluorine (1, 3,4) σ^-_{3F}=0.83; For 3 atoms of fluorine (2,3,5) σ^-_{3F}=0.89. The value of nucleophilic ortho-constant of fluorine, averaged for all polyfluorobenzenes considered above is : σ^-_o=0.21±0.03 (Table 1). From the comparison of the values σ^-_{o-F}, σ^-_{p-F}, σ^-_{m-F} it follows that electrono-withdrawing effect of fluorine atoms as a substituent on the reaction center in benzene ring in the reactions of nucleophilic substitution increases with the transition from para-to ortho- and meta- positions of fluorine with respect to substituted group: para < ortho < meta. The authors of Refs. 25,26 came also to the similar conclusion. They, however, did not define numerical value of nucleophilic ortho-constant and

fluorine atom constants in benzene ring. Using $\Sigma\sigma_i^-$ found by additivity, one can calculate reaction constants for the large range of polyfluorobenzenes $C_6F_nH_{6-n}$ with sodium methoxide, including those, whose data on reactivity are absent in the literature. The results are given in Table 2. Calculated reaction rate constants differ by 6-82% from the experimental ones. Precision of calculated reaction rate constants is limited with variations of $\sigma_o^- \pm 0.03$, with the transition from one polyfluorobenzene to another and is due to the changes in ortho-effect.

To predict the nucleophilic orientation in the reactions of polyfluorobenzenes various methods are proposed, including the method of molecular orbitals [27] by the stability analysis of the transition states [28], some of them are considered in details in [29]. All these methods, however, are of a qualitative character and don't allow to calculate the values of reaction rate constant on predicted reaction center.

Using the Hammett equation and the values of nucleophilic constants of fluorine atom groups, one can calculate rate constants of substitution reactions of fluorine with methoxide for all positions of fluorine in benzene ring of di-, tri-, tetra-, penta- fluorobenzenes and thus determine the main direction of nucleophilic substitution in these compounds (Table 2). Relative reactivity of fluorine atoms at different positions of polyfluorobenzene ring is defined from the reaction rate ratio calculated for those positions in the above way. For pentafluorobenzene this ratio is : ortho : meta:para= 8:1:93; for 1,2,3,4- tetrafluorobenzene $F_1:F_2$= 1:12; for 1,2,3,5- tetrafluorobenzene $F_1:F_2:F_5$ = - 752:1:66, i.e., it corresponds to practically observed orientation of nucleophile in the reactions of these polyfluorobenzenes with sodium methoxide [15-17,20]. Since the yields of substitution products on the various reaction center of polyfluorobenzenes will be proportional to the values of reaction rate constants in every center, one can

also define the composition of the reaction mass from the correlation calculated above. It is natural that calculated in this way distribution of products is true, if we have the ratio of reagent: substrate = 1:1. In the case of reagent excess the correlation between the products will change due to successive-parallel reactions and formation of di- and tri- substitution products.

Thus the direction of fluorine atom substitution with nucleophile in polyfluorobenzene reactions with sodium methoxide coincides with the direction of maximum electrono-withdrawing effect of the remained atoms in polyfluorobenzene and can be calculated. According to the calculation, reactivity of 1,2,4,5-tetrafluorobenzene is the least in the series of the following polyfluorobenzenes: C_6F_6 > C_6F_5H > > 1,2,3,5-$C_6F_4H_2$ > 1,2,3,4-$C_6F_4H_2$ > 1,2,4,5-$C_6F_4H_2$ (Table 2). Reaction rate constants of these compounds with sodium methoxide are related to each other as: 6320:1660:98:36:1, i.e., the reactivity of polyfluorobenzene decreases with the decrease in the number of fluorine atoms in benzene ring and primarily those which are in meta- and then ortho- position to the fluorine atom substituted by nucleophile. Reactivity of tri- and di- fluorobenzenes decreases in the following way: trifluorobenzenes: 1,3,5>1,2,3>1,3,4;difluorobenzenes: 1,3 > 1,2 > 1,4. With the transition from polyfluorobenzenes with the general formula $C_6F_nH_{6-n}$ to pentafluorobenzenes of the series C_6F_5R the prediction of the orientation of nucleophile according to the suggested technique is complicated in some cases by the following conditions: 1) absence of ortho--constant values of some substituents, R 2) absence of data on the influence of the total electrono-withdrawing effect of 4F on σ^- of substituents R 3) tendency of some substituents R to interact with nucleophile in initial and transition states, the intensity of this interaction depending on the nature of solvent and reagent [29-32].

Nucleophilic Constants of Fluorine Groups σ^-_{3F}, σ^-_{4F}, σ^-_{5F} and σ^-ortho-F from the Data on the Reaction Kinetics of $C_6F_nH_{6-n}$ with Sodium Methoxide[5,6]

Table 1

Substrate	Direction of nucleophilic substitution	Rate constants $k \cdot 10^6$ $l \cdot mol^{-1} \cdot sec^{-1}$	$\Sigma\sigma_i^-$	Nucleophilic constants of fluorine groups $\sigma^- = \frac{lgk/k_o}{\rho}$	Nucleophilic constant of ortho-fluorine
C_6F_6	All 1-6 atoms of F are equivalent	316 [6]	$2\sigma^-_o+2\sigma_m+\sigma^-_p$	1.14	0.202
C_6F_5H	In para to H [6,10,11]	80 [6]	$2\sigma_o+2\sigma_m$	1.06	0.192
1,2,3,4-$C_6F_4H_2$	F_2 and F_3 [12]	1.8 [5]	$2\sigma^-_o+\sigma_m$	0.83	0.245
1,2,3,5-$C_6F_4H_2$	F_1 and F_3 [12]	4.9 [5]	$\sigma^-_o+2\sigma_m$	0.89	0.214
1,2,4,5-$C_6F_4H_2$	All F atoms are equivalent	0.049(*	$\sigma^-_o+\sigma_m+\sigma^-_p$	$0,609\pm0.03$(**	. - σ_o average= $=0.21\pm0.03$

*) Calculated from the Hammett equation: $lgk=\rho\sigma^-+lgk_o$, where ρ (50°)=7.16. lgk_o = -11.67

**) Calculated by additivity $\sigma^-_{3F}=0.21\pm0.03+0.337+0.062=0.609\pm0.03$

Table 2

Reactions of Polyfluorobenzenes with Sodium Methoxide.
Direction of Nucleophilic Substitution in These Compound.

Substrate	Positions of F	Subst.effect in Σun. Additive val.	Subst.effect in Σun. Exp.val. (See Table 1)	Rate constants 650°C k.10⁶ l.mol⁻¹.sek⁻¹ Calc.from the Hammett eq.	Rate constants 650°C k.10⁶ l.mol⁻¹.sek⁻¹ Found	Relative mobility of P in various positions	Relative ** error of calculation in % ***
1	2	3	4	5	6	7	8
C_6F_6	all 1-6	1.156	1.141	404	316 [6]	1	28
C_6F_5H	1 and 5	0.946	-	12.7	-	8.1	-
	2 and 4	0.819	-	1.6	-	1	-
	3	1.094	1.057	145	79.5 [6]	92.6	82
1,2,3,4-$F_4C_6H_2$	1 and 4	0.609	-	0.0492	-	1	
	2 and 3	0.757	0.827	0.564	1.8 [5]	11.5	
1,2,3,5-$F_4C_6H_2$	1 and 3	0.884	0.888	4.6	4.9 [5]	752	6.1
	2	0.482	-	0.0061	-	1	-
	5	0.736	-	0.4	-	66	-

1	2	3	4	5	6	7	8
1,2,4,5-$F_4C_6H_2$	1,2,4,5	0.609	-	0.0492(50°) 0.29* (50°) 18.3 (100°) 1673 (150°)	-	1	-
1,3,5-$F_3C_6H_3$	1,3,5	0.674	-	0.14 (50°) 45.6 (100°) 3720 (150°)	-		-
1,2,3-$F_3C_6H_3$	1 and 3	0.547	-	7.7 (100°) 780 (150°)	-	5.9	-
	2	0.420	-	1.3 (100°) 164 (150°)	-	1	-
1,2,4-$F_3C_6H_3$	1	0.272	-	0.164(100°) 26.7 (150°)	-	1	-
	2	0.547	-	7.7 (100°) 780 (150°)	-	47	-
	4	0.399	-	0.97 (100°) 127 (150°)	-	6	-
1,4-$F_2C_6H_4$	1,4	0.062	-	0.009(100°) 2.0 (150°) 150 (200°)	-	1	-
1,2-$F_2C_6H_4$	1,2	0.21	-	0.07 (100°) 12.5 (150°) 750 (200°)	-	1	-

1	2	3	4	5	6	7	8
$1,3\text{-}F_2C_6H_4$	1 and 3	0.337	-	0.4 (100°) 60 (150°) 3010 (200°)	-	1	-

* Calculated from the Hammett equation[2] for reaction series (m-,p-) $RC_6H_4F+CH_3ONa(CH_3OH)$ ($t°C, \rho, \lg k_o$: 100, 6.08, -8.44; 150, 5.33, -6.03; 200, 4.75, - 4.12)

** Calculated by the authors of Ref. 26

*** $(\frac{k_{calc.}}{k_{exp.}} - 1) \cdot 100$ at 50°C

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THE KINETICS AND MECHANISM OF DIENE CONDENSATION OF HEXACHLOROCYCLOPENTADIENE WITH CYCLIC DIENOPHILES

XXII. Relative Reactivity of 5,5-dimethoxytetrachlorocyclopentadiene with endo- and exo-Anhydrides of Bicyclo/2.2.1/-5-heptene-2,3-dicarboxylic Acids

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The kinetics of diene condensation for 5,5-dimethoxytetrachlorocyclopentadiene (5,5-DMOTCCPD) with endo- and exo-anhydrides of bicyclo/2.2.1/-5 heptene-2,3-dicarboxylic acid has been studied by polarographic method at 100-130°C in chlorobenzene. The 5,5-DMOTCCPD and HCP reactivities with those of anhydrides were compared. The reactivity of 5,5-DMOTCCPD in the Diels-Alder reaction was found to be four times that of HCP. The common character of both dienes in this reaction has been shown. The general isokinetic dependence was shown to hold.

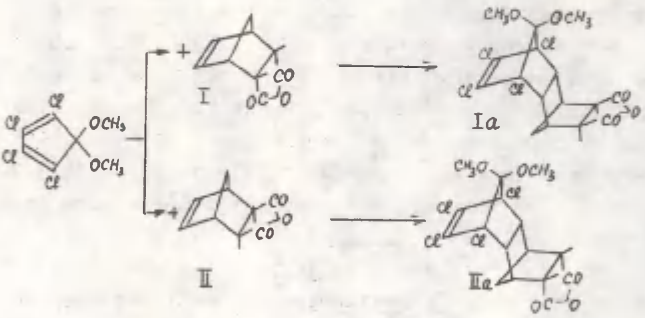
In earlier studies we knew that the reaction rate of diene condensation of hexachlorocyclopentadiene (HCP) with anhydride of exo-bicyclo/2.2.1/-5-heptene-2,3-dicarboxylic acid (exo-BHDA) was two times that with endo-BHDA[1]. This was accounted for by electron-seeking effect of endo-anhydride ring to be stronger than that of exo-anhydride group due to the field effect in the case of endo-isomer.

It was of interest for us to check the realization of the regularity observed for the reaction of these anhydrides with 5,5-dimethoxytetrachlorocyclopentadiene (5,5-DMOTCCPD) which is less electron-seeking diene than HCP, and also

to establish the quantitative relationship of reactivity for both dienes in the reaction studied.

With this aim in view the reaction kinetics of diene condensation of 5,5-DMOTCCPD with anhydrides of endo- and exo-BHDA has been examined. As in earlier work[2] we used the polarographic method to follow the concentration change of 5,5-DMOTCCPD in the reaction mixture with time. Special experiments have shown that the starting anhydrides, their adducts with 5,5-DMOTCCPD, and chlorobenzene taken as a solvent do not affect the polarography.

The reaction rate of 5,5-DMOTCCPD with anhydrides of endo-(I) and exo-(II)-BHDA (according to scheme 1) was studied at 100-130°C with a 2:1 ratio of diene to dienophile during 6 hours.



Scheme 1

The reaction was shown to be described by the second order kinetic equation (for irreversible reactions).

$$W = k_2 [5,5\text{-DMOTCCPD}] [\text{Anhydride}]$$

The rate constants were calculated according to the formula:

$$k_2 = \frac{4,606}{a\tau} \lg \frac{a-x}{a-2x} \qquad (1)$$

where a is the starting concentration of 5,5-DMOTCCPD in moles; τ is time in seconds; x is amount of 5,5-DMOTCCPD reacted during τ time (in moles).

The rate constants for this reaction with anhydrides (I) and (II) determined from 3-4 parallel runs are collected in Table 1.

Table 1

Rate Constants for Diene Condensation of 5,5-DMOTCCPD with Anhydrides of endo-(I) and exo-(II)-BHDA in Chlorobenzene

Cpd.	$k_2 \cdot 10^6$, l/mol·sec, at t, °C			
	100	110	120	130
I	7.10±0.29	12,68±1,45	22.39±0.41	38.98±0,16
II	12.85±0.21	22.58±0.53	38.87±0.69	68.47±0.82
k_{II}/k_I	1.81	1.78	1.74	1.76

As can be seen from these data the reaction rate of 5,5-DMOTCCPD with exo-anhydride of BHDA (II) is 1.7-1.8 times that with endo-anhydride (I).The same rate increase was observed in the case of exo-anhydride for the reaction with HCP in nitrobenzene[1].

The rate constants of anhydrides (I) and (II) with 5,5-DMOTCCPD which were obtained at different temperatures obey the Arrhenius equation:

$$\lg k = \lg A - E_a/4.576T \qquad (2)$$

Parameters of this equation estimated by the least-squares method are summarized in Table 2.

Table 2

Parameters of Equation (2) for Diene Condensation of 5,5-DMOTCCPD with Anhydrides (I) and (II) in Chlorobenzene

Cpd.	lgA	E_a, kcal/mol	r	S_o	n
I	4.66±0.32	16.79±0.12	0.998	0.018	4
II	4.69±0.47	16.43±0.18	0.997	0.027	4

As could be expected the activation energies (E_a) and preexponentials (lgA) of the reactions studied differ insig-

nificantly from one another for endo- and exo-anhydrides. The same case is observed when comparing the thermodynamic parameters of activation estimated by least-squares method from the equation $y = ax + b$, where $y = R\ln k/T$, $a = \Delta H^{\neq}$, $b = R\ln k/T + \Delta S^{\neq}$, $x = 1/T$. These parameters are given in Table 3.

Table 3

Thermodynamic Parameters for Activation of Diene Condensation of 5,5-DMOTCCPD with Anhydrides (I) and (II) in Chlorobenzene.

Cpd.	$\Delta H^{\neq}$ kcal/mol	$-\Delta S^{\neq}$, e.u.	r	S_o	$\Delta F^{\neq}$(388°K) kcal/mol
I	16.05±0.51	39.66±1.31	0.999	0.077	31.44
II	15.68±0.54	39.47±1.38	0.999	0.081	30.99

Previously[3] we have shown that the rate of these reactions depends insignificantly on a solvent nature. Thus, we can compare kinetic data obtained for anhydrides (I) and (II) with HCP in nitrobenzene and with 5,5-DMOTCCPD in chlorobenzene. Table 4 lists correlations of rate constants for the corresponding reactions ($k_{5,5\text{-DMOTCCPD}}/k_{HCP}$) at different temperatures.

Table 4

Correlations of Rate Constants ($k_{5,5\text{-DMOTCCPD}}/k_{HCP}$) at Different Temperatures

Cpd.	110	120	130	Mean
I	$\frac{12.68}{2.55}=4.97$	$\frac{22.39}{5.10}=4.39$	$\frac{38.98}{9.58}=4.09$	4.48
II	$\frac{22.58}{4.45}=5.07$	$\frac{38.87}{8.84}=4.40$	$\frac{68.47}{16.77}=4.08$	4.52

As one can see from the data of Table 4 the reaction rate for 5,5-DMOTCCPD is 4-5 times that of HCP. It is noteworthy that when temperature rises, the difference in reaction rates for dienophiles decreases regularly as evidenced by the dependence $\lg k_{5,5\text{-DMOTCCPD}}/k_{HCP} = f(1/T)$ (See Figure 1).

The straight line of this dependence intersects the X-axis in the point corresponding to 483°K. At this temperature the rates of dienes studied with anhydrides (I) and (II) should be equal, indicating thus the existence of isokinetic relationship in the reaction series studied[4,5]. We have carried out Arrhenius direct reaction for compounds (I) and (II) with HCP and 5,5-DMOTCCPD in order to get confirmation of this assumption. As can be seen from Fig.2, all straight lines have a common point of intersection corresponding to isokinetic temperature 485°K.

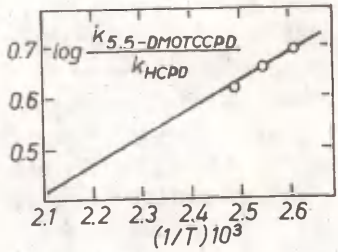


Fig.1 Logarithms of rate constant ratios ($k_{5,5DMOTCCPD}/k_{HCPD}$) vs: temperature

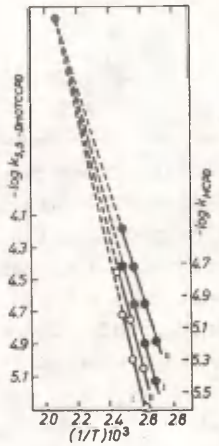


Fig.2 Logarithms of rate constants vs. reciprocal temperature for diene condensation of 5,5-DMOTCPD and HCPD with anhydrides (I) and (II).

The comparison of kinetic and thermodynamic activatinn paramaters (Table 5) for the reaction with 5,5-DMOTCCPD and HCP indicates the higher dienophilic activity of exo-anhydride over that of endo-anhydride; consequently, it is possible to speak about identical role of both dienes in the given reaction.

The higher activity of 5,5-DMOTCCPD over that of HCP

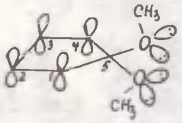
points out its less nucleophilic ability in this reaction, that is due to the partial absorption of ring electron deficit by geminal methoxy- groups.

Table 5

Activation Parameters for the Reaction of Compounds (I) and (II) with 5,5-DMOTCCPD and HCP

Diene	Cpd.	IgA	E_a kcal/mol	$\Delta H^{\neq}$ kcal/mol	$-\Delta S^{\neq}$ eu	$\Delta F^{\neq}$ kcal/mol
5,5-DM OTCCPD	I	4.66	16.79	16.05	39.66	31.44(388°K)
	II	4.69	16.43	15.68	39.47	30.99(388°K)
HCP	I	6.21	20.70	20.02	32.44	33.42(413°K)
	II	6.66	21.06	20.33	30.55	32.94(413°K)

From examination of 5,5-DMOTCCPD model it follows that the conformation of methoxy-groups, providing the planarity of C_1-C_5-O-CH_3 and C_4-C_5-O-CH_3 fragment bonds, is needed for maximum participation of unshared electron pairs of oxygen atoms in the conjugation with π-electrons of the double system.



In this case the energy barrier of rotation around C_5-O-CH_3 bonds increases and the conformation stabilization is observed. This stabilization satisfies the conditions of the maximum overlap of p_π-electron cloud of oxygen by π-regions of ring double bonds. This favors the closest approach of diene and dienophile planes in the oriented complex and, hence, the maximum overlap of their electron orbitals. The formation of such intermediate complex is more advantageous with 5,5-DMOTCCPD due to the smaller ion radius of oxygen atoms over geminal chlorine atoms in HCP. The high negative value of the activation entropy of the reaction with 5,5-DMOTCCPD (39.47 ÷ 39.66) over that of HCP (32.44 ÷ 30.55) speaks in favor of the above assumption. This value indicates the higher order of intermediate complex formed between diene and dienophile.

The lower dienophilic activity of endo-anhydride over exo-anhydride indicates that 5,5-DMOTCCPD, like HCP, is an electron-seeking addend; thus the reaction may be assumed to proceed by the mechanism of complex formation with charge transfer with the charge center being shifted from dienophile towards diene.

EXPERIMENTAL

Starting anhydrides of endo- and exo-BHDA (I) and (II) were obtained according to the known technique[7].

5,5-DMOTCCPD was synthesized by the method described elsewhere.

Diene adducte of 5,5-DMOTCCPD with endo-(I) and exo-(II) anhydrides of BHDA: anhydride (Ia) of endo-1,8,9,10-tetrachloro-11,11-dimethoxytetracyclo/6.2.2.1^{3,6},0^{2,7}/-2-dodecene-4,5-dicarboxylic acid and anhydride (IIa) of exo-1,8,9,10-tetrachloro-11,11-dimethoxytetracyclo/6.2.2.1^{3,6}, 0^{2,7}/-2-dodecene-4,5-dicarboxylic acid were prepared and identified by the method described by us[9].

The purity of the synthesized compounds was checked by thin-layer chromatography on unfixed bed of silica gel KCK in the three-component system of solvents - dichloroethane:benzene:acetic acid - 8:3:2. The development was carried out in UV-light.

Chlorobenzene was purified as in[10].

R E F E R E N C E S

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KINETICS AND MECHANISM OF DIENE CONDENSATION OF HEXACHLOROCYCLOPENTADIENE WITH CYCLIC DIENOPHILES

XXXI. Relative Reactivity of N-Phenyl- and N-Benzyl Imides of Cyclic 1,2-Dicarboxylic Acids.

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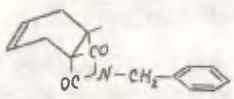
The reaction rates for diene condensation of hexachlorocyclopentadiene (HCP) with N-benzyl imides of cis-4-cyclohexene-, cis,cis-3-methyl-4-cyclohexene- and endo-bicyclo/2.2.1/-5-heptene-2,3-dicarboxylic acids in nitrobenzene are investigated. The activation parameters of these reactions are determined. In comparing the values of rate constants for the reactions studied with those for N-phenyl imides of the corresponding acids the slight decrease in the reaction rates is observed when introducing a methylene group between nitrogen and phenyl radical.

According to the donor-acceptor theory, the increase in nucleophilicity of reaction center in dienophiles of a reaction series leads to the increase in their reactivity under diene condensation with hexachlorocyclopentadiene (HCP)[1-2] and the decrease in that with cyclopentadiene[3]; alternatively, increasing electrofilicity of dienophile double bond favors the decrease in dienophilic activity in the reaction with HCP and the increase in that with cyclopentadiene. We repeatedly have paid attention to the implementation of this regularity in the case of diene condensation of HCP with N-substituted imides containing electron-donor and electron-acceptor substituents and pointed out

the electron effect transfer through N-aryl imide ring[4-6]. The effect of phenyl ring on dienophilic activity is of great importance in the imides of cis-4-cyclohexene-1,2-dicarboxylic acids (cis-4-CHDA) which has, according to our data[7], the property of electron-donating group as compared with unsubstituted imide of this acid. Thus, $k_{N-C_6H_5}/k_{N-H}$ accounts to about 1.25 ± 0.03 for the reaction of HCP with corresponding imides of cis-4-CHDA (at 130°C - 1.18; at 140° 1.28; at 150° - 1.31). The small value of this ratio can be explained by the inhibition of conjugation of phenyl ring π-electrons with unpaired electrons of bridged nitrogen because of disarrangement of imide and phenyl rings coplanarity that is due to the steric hindrance between carboxylic groups and ortho-hydrogen of the corresponding rings.

It was of interest to follow changes in dienophilic activity through the imides with a methylene group between nitrogen and phenyl ring in which the inhibition of conformation through N-C bond is absent. With this end in view we have selected N-benzyl imides of cis-4-cyclohexene-1,2- (I), cis,cis-3-methyl-4-cyclohexene-1,2- (II) and endo-bicyclo-/2.2.1/-5-heptene-2,3- (III) dicarboxylic acids which react with HCP in close spatial forms[8].



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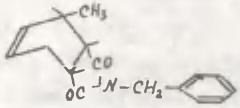

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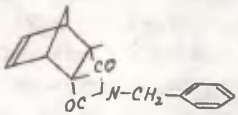
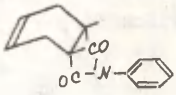


III

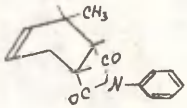
The kinetics of diene condensation of HCP with benzyl imides (I-III) in nitrobenzene has been studied by polarography through changes in diene concentration in the reaction mixture with time as it was stated in our works[4,9-11].

Table 1 lists the values of rate constants of these reactions for temperatures of 110 to 160°C estimated as mean values from 2 to 3 parallel runs.

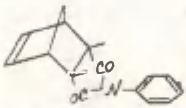
Table 1 also gives the rate constants for the reaction of HCP with N-phenyl imides (Ia-IIIa) of the corresponding acids taken from our previous works. It is apparent from the data in Table 1 that methylene group in imides (I-III) has an effect on their reactivities.



Ia



IIa



IIIa

The comparison of rate constants for benzyl imides (I, II, III) with those of the corresponding N-phenyl imides (Ia,IIa,IIIa) shows the relative constancy of the ratio $k_{\text{phenyl imide}}/k_{\text{benzyl imide}}$ amounted to 1.03 to 1.32 (Table 1) within temperature range of 110 to 160°C. At the same time the activation parameters of the reactions given which were determined from their obeying the Arrhenius equation are almost equal (see Table 2).

The higher dienophilic activity of N-phenyl imides (I-III) as compared with the corresponding N-benzyl imides (Ia-IIIa) is due to the partial transfer damping of the induction effect of phenyl radical on the reaction center through a methylene group.

Thus, the methylene group, located between an aromatic nucleus and nitrogen, has a negative effect on the reactivities of N-benzyl imides (I-III) studied.

Table 1

Rate Constants and Their Ratios for Diene Condensation of HCP with N-Benzyl (I-III) and N-Phenyl(Ia-IIIa) Imides of cis-4-cyclohexene-1,2-, cis,cis-3-methyl-4-cyclohexene-1,2- and endo-bicyclo/2.2.1/-5-heptene-2,3-Dicarboxylic Acids in Nitrobenzene

Cpd	$k_2 10^6$, l/mol·sec, at temperature t, °C					
	110	120	130	140	150	160
I	2.76±0.10	5.22±0.13	10.02±0.16	18.49±0.11	36.25±0.27	69.93±0.49
Ia	3.90±0.21	6.62±0.31	10.35±0.32	20.99±0.44	41.07±0.97	74.33±2.00
Ia/I	1.41	1.27	1.03	1.14	1.32	1.06
II	6.03±0.33	11.17±0.20	20.45±0.59	38.58±0.69	73.12±1.37	136.31±4.42
IIa	6.85±0.28	13.56±0.40	24.61±0.53	44.26±0.92	82.75±0.98	154.74±1.20
IIa/II	1.14	1.21	1.20	1.14	1.13	1.13
III	5.46±0.11	10.22±0.19	17.96±0.81	37.53±0.71	70.80±0.89	122.57±0.98
IIIa	6.48±0.08	12.49±0.17	19.52±0.22	41.57±0.31	77.39±0.21	137.28±0.91
IIIa/III	1.19	1.22	1.09	1.11	1.09	1.21

Note. The values of rate constants for compounds Ia,IIa and IIIa are taken from Refs. 4,1,12, respectively.

Table 2

Activation Parameters for Diene Condensation of HCP with N-Benzyl (I-III) and N-Phenyl (Ia-IIIa) Imides of cis-4-cyclohexene-1,2-, cis,cis-3-methyl-4-cyclohexene-1,2- and endo-bicyclo/2.2.1/-5-heptene-2,3-Dicarboxylic Acids in Nitrobenzene

Cpd	Ea, kcal/mol	lgA	$\Delta H^{\neq}$ kcal/mol	$-\Delta S^{\neq}$ e.u.	$\Delta F^{\neq}$ (°K) kcal/mol
I	21.27±0.40	6.55±0.25	20.46±0.46	31.18±1.14	33.18 (408)
Ia	18.80±0.70	5.28±0.51	18.02±0.07	36.88±1.66	32.14 (398)
II	20.59±0.44	6.49±0.24	19.78±0.52	31.41±1.27	32.59 (408)
IIa	19.74±0.36	6.10±0.19	19.00±0.23	33.07±0.57	31.66 (398)
III	20.82±0.50	6.59±0.27	20.01±0.50	31.01±1.23	32.66 (408)
IIIa	19.82±0.77	6.09±0.41	19.06±0.64	33.13±1.57	31.75 (398)

It should be noted that previously[1,2,9] in the course of the investigations of kinetics of diene condensation of HCP with anhydrides and N-substituted imides of cis-4-cyclohexene-1,2-dicarboxylic acid series we observed the high reactivities of dienophiles with a methylene group in position 3 of cyclohexene fragment. This fact is observed when analyzing the data in Table 1: N-benzyl imide (II) is more reactive than N-benzyl imide (I) (about by a factor of 2) because the presence of the bowsprit methyl group has a positive induction effect on the reaction center, reinforcing thus donor-acceptor interaction of diene with dienophile.

EXPERIMENTAL

Synthesis and properties of N-benzyl imide of 4-cyclohexene-1,2-dicarboxylic acid (I) were described in our preceding work[13].

N-Benzyl imide of cis,cis-3-methyl-4-cyclohexene-1,2-dicarboxylic acid (II) was synthesized according to the preparation procedure (I)[13] from 16.6 g (0.1 mole) of anhydride of cis,cis-3-methyl-4-cyclohexene-1,2-dicarboxylic acid and 10.7 g (0.1 mole) of benzyl imide. The yield is 71%. Rf is 0.62. Anal.Calcd. for $C_{16}H_{17}NO_2$: C,75.3;H,6.67; N, 5.52. Found: C, 74.7; H, 6.83; N, 5.31.
IR-spectrum ($\Delta\nu$, cm^{-1}) C=O 1720; C=C 1610.

N-Benzyl imide of endo-bicyclo/2.2.1/-5-heptene-2,3-dicarboxylic acid (III) was obtained according to the procedure described[13] from 16.4 g (0.1 mole) of anhydride of endo-bicyclo/2.2.1/-5-heptene-2,3-dicarboxylic acid and 10.7 g (0.1 mole) of benzyl imide. The yield is 22.7 g (90%), mp 73-74°C. Rf is 0.51. Anal.Calcd. for $C_{16}H_{15}NO_2$: C, 75.89; H, 5.93; N, 5.53. Found: C, 75.63; H, 6.1; N, 5.71
IR-spectrum ($\Delta\nu$, cm^{-1}): C=O 1740, C=C 1620.

N-Benzyl imide of endo,exo-1,2,3,4,11,11-hexachlorotricyclo/6.2.1.$0^{5,10}$/-2-undecene-7,8-dicarboxylic acid (Ib)

A mixture of 4.82 g (0.02 mole) of N-benzyl imide (I)

and 10.92 g (0.04 mole) of HCP was placed into glass ampoule and heated on the oil bath at 140-150°C for 10 hr. To the end of this period the reaction mixture was cooled to 70°C, 25 ml of n-heptane was added to this mixture to extract the unreacted HCP and filtered through the Shott filter. The end-product was recrystallized from benzene yielding 9.95 g of Ib; mp 195°C. Rf is 0.67 (eluent is benzene:dichloroethane: acetic acid=40:15:1.5 by volume, adsorbent is activated Al_2O_3. Development was effected by UV-radiation).
Anal.Calcd. for $C_{20}H_{15}Cl_6NO_2$: C, 46.69; H, 2.92; Cl, 41.44; N, 2.73. Found: C, 46.95; H, 3.14; Cl, 40.74; N, 2.52.
IR-spectrum ($\Delta\nu$, cm^{-1}) C=O 1710; C=C 1610.

N-Benzyl imide of endo-exo-cis,cis-1,2,3,4,11,11-hexachloro-6-methyl-tricyclo/6.2.1.$0^{5,10}$/-2-undecene-7,8-dicarboxylic acid (IIb).

First, anhydride of endo-exo-cis,cis-1,2,3,4,11,11-hexachloro-6-methyltricyclo/6.2.1.$0^{5,10}$/-2-undecene-7,8-dicarboxylic acid was obtained according to the procedure[14]. The end-product was obtained by the procedure[13] from 3 g (0.0068 mole) of the above anhydride and 0.73 g (0.0068 mole) of benzyl amine. The yield is 94.4%, mp 155-156°C. Rf is 0.69.
Anal.Calcd. for $C_{21}H_{17}Cl_6NO_2$: C, 47.71; H, 3.22; N, 2.66; Cl, 40.34. Found: C, 47.53; H, 3.36; N, 2.83; Cl, 40.75.
IR-spectrum ($\Delta\nu$, cm^{-1}): C=O 1712; C=C 1610.

N-Benzyl imide of endo-exo-1,2,3,4,11,11-hexachlorotetracyclo/6.2.1.1.$0^{5,10}$/-2-dodecene-7,8-dicarboxylic acid(IIIb

This was obtained from 4 g (0.0158 mole) of N-benzyl imide (III) and 8.63 g (0.0316 mole) of HCP according to the conditions of preparation of compound (Ib) during 12 hr. The yield is 8.2 g (98.6%), mp 222-223°C. Rf is 0.62.
Anal.Calcd. for $C_{21}H_{15}Cl_6NO_2$: C, 47.90; H, 2.85; Cl, 40.49; N, 2.67. Found: C, 48.10; H, 2.75; Cl, 40.76; N, 2.71.
IR-spectrum ($\Delta\nu$, cm^{-1}): C=O 1730; C=C 1720; C-Cl 710-770.

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KINETICS AND MECHANISM OP DIENE CONDENSATION OP HEXACHLOROCYCLOPENTADIENE WITH CYCLIC DIENOPHILES

XXXIII*. Dienophilic Activity of N-Allyl Imides of Cyclic 1,2-Dicarboxylic Acids

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The dienophilic activity of N-allyl imides of cyclic 1,2-dicarboxylic acids in their diene condensation with hexachlorocyclopentadiene is investigated. On the basis of the kinetic data analysis the role of electron effects in dienophilic activity of N-allyl imides of ortho-phthalic, cis-4-methyl-4-cyclohexene-1,2-dicarboxylic and cyclohexane-1,2-dicarboxylic acids is shown.

In our previous works we demonstrated the role of electron effects in dienophilic activity of anhydrides[1] and imides[2] of cis-4-cyclohexene-1,2- (cis-4-CHDA) and endo-bicyclo/2.2.1/-5-heptene-2,3-dicarboxylic (endo-BHDA)[3,4] acids in the reaction of diene condensation with hexachlorocyclopentadiene (HCP).

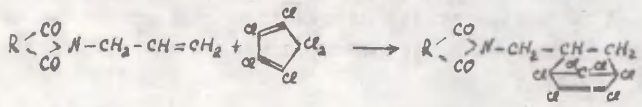
It was found that the transfer of induction effect of N-substituent in the corresponding N-aryl imides on the reaction center both through the molecule skeleton and by interaction of π-orbitale of sp^2-carbon atoms of cyclohexene and bicycloheptene rings, on the one hand, and carbonyl

* Previous communication of M.S.Salakhov and N.F.Musaeva see in "Reaction Kinetics and Catalysis Letters", 12, No.3 (1979).

groups,on the other hand, through the space, is linearly dependent on the electron nature of substituent in the aromatic ring.

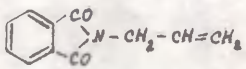
The reaction sensitivity to changes in electron-donating and electron-seeking nature of N-substituent in the imides[2,4] is indicative of p-π-transfer of the induction effect through the N-C bond of N-substituent.

In this connection it was interesting to study the effect of imide radical nature on the reactivity of N-allyl double bond in the reaction with HCP



It is known that in N-allyl imides of cyclic 1,2-dicarboxylic acids the $C_{sp}2$-$C_{sp}3$ bond (between trigonal and tetragonal carbon atoms) leads to planarity of a single bond of allyl carbon and ethylenic bond. We expected this fact and also the N-$C_{sp}3$ bond formation to assure the planar structure of N-allyl imide fragment assisting the system conjugation and thus to increase the reaction center sensitivity to changes in six-membered ring nature.

N-Allyl imides of ortho-phthalic (I), cis-4-methyl-4-CHDA (II) and cyclohexane-1,2-dicarboxylic (III) acids were taken as dienophiles.



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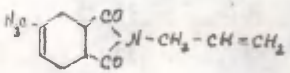

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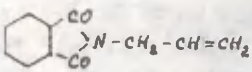


III

Since electron structures of six-membered carbon cycles of these imides differ from each other, their effects on the reaction center in the reaction with HCP were expected to be different. Such ring effects were followed by investigation of diene condensation kinetics for imids (I-III) with HCP by means of polarograpgy through changes in the wave heights of HCP reduction in the reaction mixture over the temperature range from 110 to 150°C in nitrobenzene. It was established that with a 2:1 molar ratio of diene to dienophile the reaction is of general second order as evidenced by the constancy of reaction rate constants estimated with different conversion degrees of starting substances (Table 1).

Table 1

Reaction Rate Constants for Diene Condensation of N-Allyl Imides (I-III) with HCP at Different Conversion Degrees of Starting Substances

Time, hr	I		II		III	
	Yield, %	$k_2 \cdot 10^6$ l/mol sec	Yield, %	$k_2 \cdot 10^6$ l/mol sec	Yield, %	$k_2 \cdot 10^6$ l/molsec
1	13.6	45.57	7.8	27.09	5.6	19.01
2	22.6	44.63	15.4	28.52	10.8	19.23
3	31.0	44.21	21.8	28.49	15.6	19.26
4	38.2	44.07	27.0	27.76	20.4	19.72
5	45.0	44.78	32.0	27.63	23.8	18.96
6	50.8	45.36	36.0	27.01	27.2	18.65
k_{av}	$(44.76 \pm 0.64) 10^{-6}$		$(27.74 \pm 0.69) 10^{-6}$		$(19.13 \pm 0.39) 10$	

(Solvent, nitrobenzene, T,140°C, reaction mixture volume, 10 ml. HCP, 0.009 mole, Dienophile,0.0045 mole).

Reaction rate constants for N-allyl imides studied with HCP are listed in Table 2.It is evident from the data in Table 2 that the rate constants vary depending on the dienophile structures and temperature.

The activation parameters for the reactions given were determined according to Ref. 2 from the temperature de-

pendence of rate constant logarithms, these are given in Table 3.

Table 2

Reaction Rate Constants of Diene Condensation of N-Allyl Imides (I-III) with HCP in Nitrobenzene

Cpd.	$k_2 \cdot 10^6$ l/mol·sec, at T,°C				
	110	120	130	140	150
I	8.69±0.38	15.00±0.57	25.56±0.51	44.76±0.64	76.93±0.98
II	4.77±0.25	8.55±0.07	15.46±0.29	27.74±0.69	47.79±1.85
III	3.05±0.19	5.58±0.31	10.58±0.59	19.13±0.39	34.80±0.93

Table 3

Activation Parameters for Diene Condensation of N-Allyl Imides (I-III) with HCP in Nitrobenzene at 110-150°C.

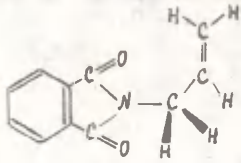
Cpd.	Ea kcal/mol	lgA	$\Delta H^{\neq}$ kcal/mol	$-\Delta S^{\neq}$ e.u.	$\Delta F^{\neq}$(403°K) kcal/mol
I	17.56±0.35	4.94±0.18	16.76±0.34	38.49±0.85	32.28
	r=9987	S=0.014	r=0.9994	S=0.065	
II	18.65±0.21	5.30±0.11	17.83±0.21	36.86±0.53	32.69
	r=0.9996	S=0.008	r=0.9993	S=0.069	
III	19.65±0.27	5.68±0.15	18.85±0.27	35.11±0.66	33.00
	r=0.9997	S=0.011	r=0.9997	S=0.050	

From the analysis of the data in Tables 1 and 2 it is seen that the variation in electron structure of six-membered ring for compounds (I-III) affects their reactivities little.

Threefold decrease in k value with transition from cpd. (I) to compound (III) is indicative of different transfer of electron effect of six-membered carbon ring on the reaction center.

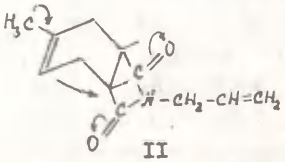
The higher reactivity of compound (I) is apparently due to the preference of planar configuration of the molecule owing to shielding of $N\text{-}CH_2$-bond by ethylene bond[6] and thus to increase polar conjugation between benzene nucleus and reaction center, since in the molecule given

the phenyl ring offers the extinction of deficient charge on the carbon atoms of carboxyl groups that is a hindrance for electron withdrawal from the reaction center. This in general leads to the conservation of electron-donating ability of the reaction center and provides the charge transfer from dienophile to electron-seeking diene according to the common mechanism of complex formation with charge transfer.



I

In the case of compound (II) the coplanarity of this ring with imide cycle is absent owing to synboat conformation of cyclohexene ring[7]. However, in this case a partial extinction of electron deficit of carbons of carboxyl groups takes place by π-electrons of sp^2-carbon atoms of cyclohexene ring through the space (field effect). Apparently therefore the withdrawal of π-electrons by carboxyl groups from allyl radical is weaker than that of benzene ring in compound (I).



II

As a result, under interaction with electron-seeking HCP the double bond in allyl imide (II) exhibits less electron-dinating property than in allyl imide (I). The charge displacement to the direction indicated is also favored by electron-donor methyl group at sp^2-carbon atom in cyclohexene ring.

On the other hand, this methyl group, as we have shown earlier[5], supresses completely the reactivity of cyclohexene ring with HCP and hence provides the realization of allyl double bond in this reaction.

This suggestion being true, it should be expected that due to the unsaturation of six-membered ring N-allyl imide of cyclohexane -1,2-dicarboxylic acid (III) will manifest the lower dienophilic activity in the reaction with HCP over that of N-allyl imide of 4-methyl-cis-4-CHDA (II).

The regularity observed in the dienophilic activity

of compounds (I-III) is also consistent with the data in Table 3 which lists the activation parameters for the reactions studied. Thus, over the temperature range from 110 to 150°C, the activation energy (E_a) increases regularly with transition from compound (I) to compound (III) and negative value of activation entropy ($\Delta S^{\neq}$) decreases regularly in the reverse direction. This is probably indicative of small order of transition complex for compound (I).

E X P E R I M E N T A L

The kinetic runs were carried out in the ampoule over the temperature range from 110 to 150 C in nitrobenzene. The reaction course was followed by changes in wave heights of HCP reduction in the reaction mixture with time (on an "OH-2" polarograph "Radelkis") against that for the starting HCP. The polarography conditions were described in the previous work[1]. The check experiments have shown that the starting N-allyl imides (I-III) and their adducts with HCP do not prevent from determining the latter. The concentration of reacting HCP was determined by

$$x = a\left(1 - \frac{H_\tau}{H_0}\right)$$

where a is the initial concentration of HCP, mol/l; H_0 and H_τ are the heights of waves for HCP reduction before the reaction start and with time τ, respectively, and τ is the time, hr. Then the bimolecular constant of reaction rate was estimated as follows

$$k_2 = \frac{4.606}{a\tau} \lg \frac{a-x}{(a-2x)}$$

The starting N-allyl imides (I-III) were obtained according to the known procedures[8,9].

N-(Methylene-1,2,3,4,7,7-hexachlorobicyclo/2.2.1/-2-heptene-phtalimide (Ia). -

A mixture from 18.8 g of N-allyl phtalimide (I) and 27.3 g of HCP was heated in the ampoule on an oil bath at 140 C for 14 hr. The reaction mixture was subjected to the

steam distillation to remove the traces of (I). Precipitated crystals were filtered from the mixture of benzene with heptane giving 41.4 g (90%) of adduct (Ia), mp 127 C, Rf is 0.80. Anal Calcd.for $C_{16}H_9Cl_6NO_2$: C 41.74; H 1.95; CI 46.39; N 3.04. Pound: C 41.55; H 1.82; CI 46.00; N 2.89

Table 4

Physico-Chemical Characteristics for N-Allyl Imides (I-III)

Cpd.	Mp °C	Bp °C	Rf	Formula	Elemental analysis,%* C	H	N
I	66		0.81	$C_{11}H_9O_2N$	70.58 / **70.10**	4.81 / 4.65	7.49 / 7.52
II		148-150 2 mm	-	$C_{12}H_{15}O_2N$	70.24 / **70.81**	7.31 / 7.15	6.83 / 6.73
III		133-135 10 mm	-	$C_{11}H_{15}O_2N$	68.39 / 67.70	7.77 / 7.50	7.25 / 7.10

* The numerator is the value calculated, the denominator is the value found.

N-(Methylene-1,2,3,4,7,7-hexachlorobicyclo/2.2.1/-2-heptene imide of 4-methyl-cis-4-cyclohexene-1,2-dicarboxylic acid (IIa).-

This was obtained according to the procedure for (Ia) synthesis from 20.5 g of N-allyl imide of 4-methyl-cis-4-cyclohexene-1,2-dicarboxylic acid (II) and 27.3 g of HCP. The yield was 41.2 g (86.2%), mp 130 C, Rf is 0.59. Anal.Calcd. for $C_{17}H_{15}Cl_6NO_2$: C 42.67; H 3.13; CI 44.56; N 2.92. Found: C 42.41; H 2.99; CI 44.50; N 2.82.

N-(Methylene-1,2,3,4,7,7-hexachlorobicyclo/2.2.1/-2-heptene) imide of cyclohexane-1,2-dicarboxylic acid (IIIa)

This was obtained similarly to (Ia) from 19.3 g of N-allyl imide of cyclohexane-1,2-dicarboxylic acid (III) and 27.3 g of HCP. The yield was 41.6 g (89.2%) of wax-like product. Rf is 0.61. Anal.Calcd. for $C_{16}H_{15}Cl_6NO_2$: C 41.20; H 3.21; CI 45.70; N 3.00. Found: C 41.01; H 3.00; CI 45.38; N 2.88.

The purity of the starting and synthesized products

was checked by thin-layer chromatography with unfixed layer of a sorbent according to Ref.3.

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KINETICS AND MECHANISM OP DIENE CONDENSATION OF HEXACHLOROCYCLOPENTADIENE WITH CYCLIC DIENOPHILES

XXVI. Synthesis and Kinetics of Formation of Diene Adducts of Hexachlorocyclopentadiene with N-glycidyl Imides of 4-Cyclohexene-1,2- and Bicyclo/2.2.1/-5-heptene-2,3-Dicarboxylic Acids

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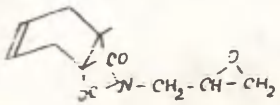
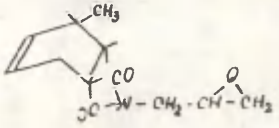
The kinetics of diene condensation of hexachlorocyclopentadiene (HCP) with N-glycidyl imides of 4-cyclohexene-, cis,cis-3-methyl-4-cyclohexene-1,2-dicarboxylic and also endo- and exo-bicyclo/2.2.1/-5-heptene-2,3-dicarboxylic acids was studied in nitrobenzene. The comparative analysis of kinetic data with those for N-phenyl imides of the corresponding acids in the reaction with HCP has shown that N-glycidyl group is a stronger electron-donating group than a phenyl radical. The existence of an isokinetic relationship for compounds studied was verified.

The results of investigation of diene condensation of hexachlorocyclopentadiene (HCP) with N-glycidyl imides (I-IV) of 4-cyclohexene-1,2- (4-CHDA) and bicyclo/2.2.1/-5-heptene-2,3-dicarboxylic (BHDA) acids are presented in this paper.



I



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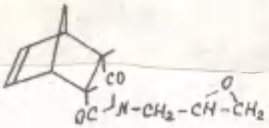

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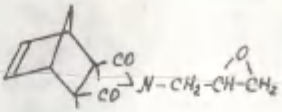
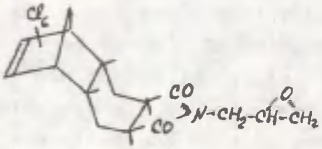
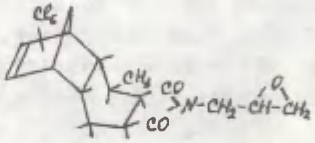


IV

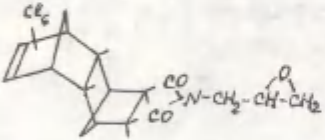
Due to stereospecific course of the Diels-Alder reaction between HCP and imides of cis-4-CHDA, cis,cis-3-Me-4-CHDA snd endo- snd exo-BHDA[1,2] the formation of one spatial adduct from each N-glycidyl imide (I-IV),respectively, should be expected.



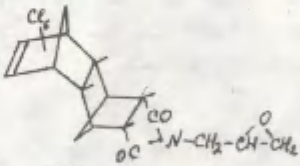
Ia



IIa

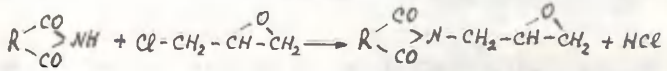


IIIa

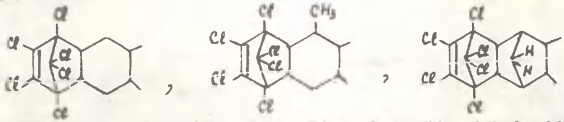


IVa

The identity of properties of N-glycidyl imides obtained by counter-synthesis-interaction of imides of the corresponding acids with epichlorohydrin in the presence of alkali metal carbonates[3] evidences in favor of the above assumption



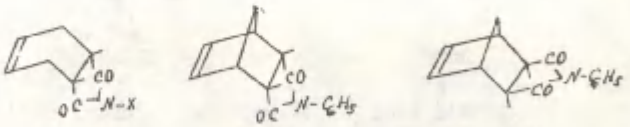
where R is



The investigation results show the high dienophilic activity of N-glycidyl imides (I-IV) studied which leads to good yields of the corresponding adducts (Ia-IVa) at relatively low temperatures (100 to 120°C) as compared with those (150 to 160°C) required for other N-substituted imides of 4-CHDA.

Accordingly, we decided to obtain qualitative data concerning with the reactivity of dienophilee (I-IV) and elucidate the role of glycidyl radical in these compounds.

With this end in view the kinetics of diene condensation of HCP with N-glycidyl imides (I-IV) of 4-CHDA and BHDA in nitrobenzene was studied by polarographic control of the HCP consumption. The values of rate constants and activation parameters for the above reactions are summarized in Tables 1 and 2.The values for the reactions of N-unsubetituted (V,VI) and N-phenyl imides (VII,VIII) of 4-CHDA and BHDA (IX-X) with HCP in nitrobenzene[4-7] are also presented.



V-VIII IX X

where R=X=H(V); R=CH_3, X=H(VI); R=H, X=C_6H_5(VII);

R=CH_3, X=C_6H_5(VIII).

As can be seen from Table 1 the reaction rate of glycidyl imides (I-IV) studied is higher than that of N-unsubstituted (V,VI) and N-phenyl imides (VII-X). Thus, N-glycidyl imide of cis-4-CHDA (I) is five times as active as

Table 1

Rate Constants* of Diene Condensation of HCP with N-Substituted Imides of 4-CHDA and BHDA Series in Nitrobenzene

Cpd.	$k_2 \cdot 10^5$, l/mol·sec at t, °C				
	80	90	100	110	120
I	3.15±0.08	5.36±0.24	9.22±0.38	15.64±0.16	25.63±0.13
II	6.04±0.10	9.97±0.15	17.77±0.78	31.08±0.53	52.60±0.83
III	5.86±0.21	9.88±0.13	16.79±0.19	27.65±0.38	45.80±0.36
IV	10.27±0.14	16.00±0.19	25.94±0.25	44.18±0.35	77.38±0.39
V	-	-	-	2.43±0.14	4.62±0.21
VI	-	-	1.69±0.13	3.34±0.24	6.12±0.24
VII	-	-	2.01±0.11	3.90±0.21	6.61±0.31
VIII	-	-	3.53±0.12	6.85±0.28	13.56±0.40
IX	-	-	-	6.48±0.08	12.49±0.17
X	-	-	-	11.45±0.15	22.40±0.28

Cpd.	$k_2 \cdot 10^5$, l/mol·sec at t, °C			
	130	140	150	160
I	44.73±0.53	76.69±0.74	-	-
II	78.79±0.31	121.24±2.11	-	-
III	69.69±0.98	118.47±1.29	-	-
IV	122.71±0.63	189.36±4.36	-	-
V	8.73±0.52	16.27±0.72	31.30±0.64	58.53±0.78
VI	10.83±0.53	17.51±0.29	34.51±0.87	65.57±0.91
VII	10.35±0.32	20.99±0.44	41.07±0.97	74.33±2.00
VIII	24.61±0.53	44.26±0.92	82.75±0.98	154.74±1.20
IX	19.52±0.22	41.57±0.31	77.39±0.21	137.28±0.91
X	35.16±0.34	69.01±1.72	126.97±1.00	213.69±1.55

* The arithmetic mean values for constants with root-mean-square error are given.

Table 2

Kinetic and Thermodynamic Activation Parameters for Reaction of Diene Condensation of HCP with N-Substituted Imides of 4-CHDA and BHDA Series in Nitrobenzene

Cpd.	E_a kcal/mol	lgA	r	S	$\Delta H^{\neq}$ kcal/mol	$-\Delta S^{\neq}$ e.u.	r	S	$\Delta F^{\neq}$(398°K kcal/mol
I	15.40±0.40	3.97±0.23	0.998	0.032	14.66±0.37	42.77±0.96	0.998	0.133	31.04
II	14.81±0.24	3.91±0.14	0.999	0.019	14.06±0.23	43.06±0.61	0.999	0.084	30.56
III	14.48±0.11	3.70±0.06	0.999	0.009	13.71±0.22	44.15±0.57	0.999	0.079	30.62
IV	14.39±0.42	3.88±0.24	0.998	0.033	13.67±0.48	43.29±1.25	0.997	0.173	30.25
V	20.56±0.37	6.09±0.20	0.999	0.020	19.80±0.29	33.13±0.73	0.999	0.076	32.48
VI	18.83±0.44	5.24±0.24	0.999	0.032	18.05±0.39	37.05±0.98	0.998	0.132	32.24
VII	18.80±0.70	5.28±0.38	0.996	0.051	18.02±0.67	36.88±1.66	0.996	0.222	32.14
VIII	19.74±0.36	6.10±0.19	0.999	0.026	19.00±0.23	33.07±0.57	0.999	0.075	31.66
IX	19.82±0.77	6.09±0.41	0.997	0.043	19.06±0.64	33.13±1.57	0.997	0.163	31.75
X	18.93±0.57	5.85±0.30	0.998	0.032	18.15+0.47	34.31+1.15	0.998	0.120	31.29

imide of cis-4-CHDA (V) and four times as active as N-phenyl imide of cie-4-CHDA (VII) within temperature range of 130 to 140°C. Similarly under these conditions N-glycidyl imide of ois,cis-3-Me-4-CHDA (II) is more reactive than the corresponding imide (VI) (by a factor of 7) and than N-phenyl imide (VIII) (by a factor of 3). endo-(III) and exo-(IV) N-Glycidyl imides are more active as dienophiles than the corresponding endo-(IX) and exo-(X) N-phenyl imidee of BHDA (by a factor of 3). Thus, the comparison of the reaction rate for HCP with imides studied shows that N-glycidyl group ie a stronger electron-donating group than the phenyl radical which favors a charge displacement from dienophile to diene[4-7].

It is interesting to note that in accordance with our previous observations[6,9,10] N-glycidyl imide of cis,cis-3-Me-4-CHDA is more active than similar imide without methyl group (by a factor of 1.5 to 2) as evidenced by positive induction effect of this group. Furthermore, the stronger dienophilic activity of exo-N-glycidyl imide of BHDA (IV) over that of endo-snalogue (III) is observed to be retained.

It is noteworthy that the higher dienophilic activity of N-glycidyl imides (I-IV) as compared with imides (V-X) is observed also for the values of activation parsmeters (Table 2).

In the investigation of the dependence of rate constant logarithms (lgk) on the reciprocal temperature (Fig.1) the pairs of straight lines have a common point of intersection: the temperature range of 580±30°K.

It is evident from the analysis of data in Table 3 that other methods of determination of isokinetic temperature (β) also give the values of the same order in terms of $lgk_{140}-lgk_T$ (Fig.2), $\Delta H^{\neq} - \Delta S^{\neq}$ (Fig.3), $lgA-E_a$ (Fig.4) and $\Delta H^{\neq} - \Delta F^{\neq}$ (Fig.5).

The existence of isokinetic relationship with the mean temperature $\beta = 617 \pm 25°K$ assumes a single reaction mechanism for HCP with N-substituted imides of 4-CHDA and BHDA

Table 3

Correlation Parameters for Equations y=ax+b of Kinetic and Activation Parameter Dependences for Diene Condensation of HCP with N-Substituted Imides of 4-CHDA and BHDA Series

Eqn.	x	y	a	b	r	e	n	β, K
1	$lgk_{100°C}$		0.8154±0.045	-0.0085±0.2318	0.992	0.054	7	785
2	$lgk_{110°C}$		0.8485±0.042	-0.0358±0.2090	0.990	0.055	10	735
3	$lgk_{120°C}$	lgk_{140}	0.8829±0.029	-0.0889±0.1420	0.995	0.038	10	669
4	$lgk_{130°C}$		0.9280±0.034	-0.0759±0.1535	0.994	0.041	10	607
5	$lgk_{140°C}$		0.8977±0.026	0.0762±0.1175	0.998	0.015	6	753
6	$lgk_{150°C}$	lgk_{160}	0.9394±0.025	0.0022±0.109	0.998	0.014	6	683
7	$\Delta S^{\neq}$	$\Delta H^{\neq}$	0.5140±0.035	36.38±1.321	0.982	0.494	10	514
8	lgA	E_a	2.3586±0.159	5.749±0.800	0.982	0.496	10	515
9	$\Delta F^{\neq}$	$\Delta H^{\neq}$	2.8748+0.495	-73.953+15.540	0.897	1.150	10	587

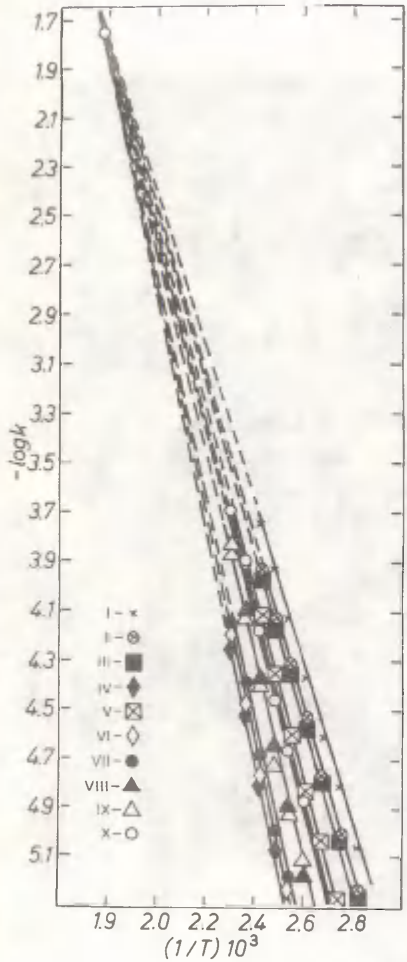


Fig.1 Dependence of logarithms of rate constants on reciprocal temperature

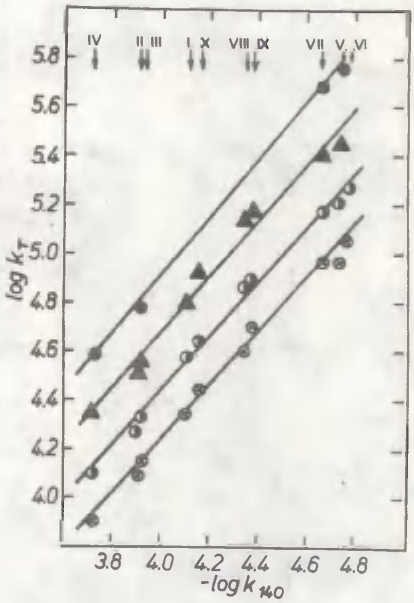


Fig.2 Dependences of logarithms of rate constants for reactions of compounds (I-X) with HCP at temperatures: 100-140°C - ● ; 110-140°C - ▲ ; 120-140°C - ◑ ; 130-140°C - ⊗ .

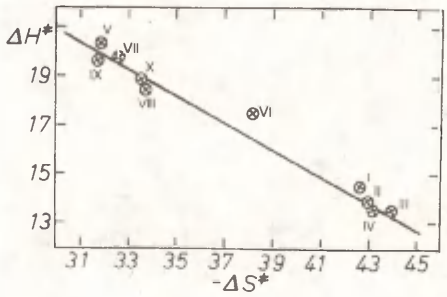


Fig.3 Activation enthalpy (ΔH^{*}) as a function of activation entropy (ΔS^{*}) for reaction of HCP with compounds (I-X).

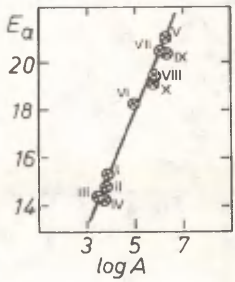


Fig.4 Activation energy (E_a) vs. pre-exponential (lgA) for the reaction of HCP with compounds (I-X).

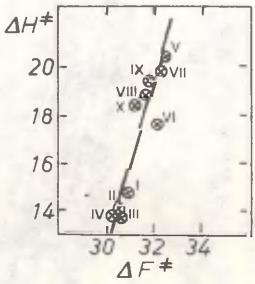


Fig.5 Activation enthalpy (ΔH^{*}) vs. free energy of activation (ΔF^{*}) for the reaction of HCP with compounds (I-X).

series in nitrobenzene.

EXPERIMENTAL

The initial N-glycidyl imides of 4-CHDA and BHDA (I-IV) were obtained and characterized by some of us[2].

The adducts (Ia-IVa) of N-glycidyl imides (I-IV) with HCP were synthesized as follows.

endo-exo-N-Glycidyl imide of 1,2,3,4,11,11-hexachloro-tricyclo/6.2.1.$0^{5,10}$/-2-undecene-7,8-dicarboxylic acid(I): a mixture of 20.7 g (0.1 g-mol) of N-glycidyl imide of 4-cyclohexene-1,2-dicarboxylic acid,54.6 g (0.2 g-mol) of HCP and 30 ml of dry toluene was refluxed during 6 hours at 120-125°C. After cooling the main product was precipitated by petroleum ether. The yield of adduct (Ia) was 38.4 g (80% of theory),mp 186-187°C (from acetone), Rf is 0.53. Anal.Calcd.for $C_{16}H_{13}C_3NCl_6$: C 40.0; H 2.70; N 2.91; CI 44.38. The content of epoxy groups is 8,96%. Pound: C 40.6; H 2.68; N 2.87; CI 43.96. The content of epoxy groups is 8.78%.

endo-endo-trans,cis-N-Glycidyl imide of 1,2,3,4,11,11-hexachloro-6-methyltricyclo/6.2.1.$0^{5,10}$/-2-undecene-7,8-dicarboxylic acid (IIa): was obtained under conditions similar to those for adduct (Ia) from 22.1 g (0.1 g-mol) of N-glycidyl imide (II) 54.6 g (0.2 g-mol) of HCP and 30 ml of toluene. The yield of IIa was 39.52 g (80% of theoretical), mp 111-112°C (from methanol) Rf is 0.64. Anal.Calcd.for $C_{17}H_{15}O_3NCl_6$: C 41.29; H 2.83; CI 43.11; N 2.83. The content of epoxy groups is 8.70%. Pound: C 41.22; H 3.34; N 2.80; Cl 43.04. The content of epoxy groups is 8.58%.

endo-endo-N-Glycidyl imide of 1,2,3,4,11,11-hexachlorocyclo/6.2.1.$0^{5,10}$/-2-dodecene-7,8-dicarboxylic acid (IIIa) : was obtained according to the synthesis of adduct (Ia) from 21.9 g (0.1 g-mol) of endo-N-glycidyl imide of bicyclo/2.2.1/-5-heptene-2,3-dicarboxylic acid (III),54.6 g (0.2 g-mol) of HCP and 20 ml of toluene. The yield is

41.8 g (85% of theoretical),mp 205-207°C (from acetone), Rf ie 0.33. Anal.Calcd.for $C_{17}H_{18}O_3NCl_6$: C 41.46; H 2.64; N 2.84; CI 43.23. The content of epoxy groups is 8.74%. Pound: C 41.42; H 2.60; N 2.80; CI 43.10. The content of epoxy groups is 8.26%.

endo-exo-N-Glycidyl imide of 1,2,3,4,11,11-hexachlorotetracyclo/6.2.1.1.$0^{5,10}$/-2-dodecene-7,8-dicarboxylic acid (IV): was obtained according to the 1a synthesis from 21.9 g (0.1 g-mol) of exo-N-glycidyl imide of bicyclo /2.2.1/-5-heptene-2,3-dicarboxylic acid (IV), 54.6 g (0.2 g-mol) of HCP and 20 ml of toluene. The yield is 41.8 g (85% of theoretical), mp 238.5-239°C (from acetone), Rf is 0.33. Anal.Calcd.for $C_{17}H_{13}O_3NCl_6$: C 41.46; H 2.64; N 2.84 Cl 43.23. The content of epoxy groups is 8.74%. Found: C 41.44; H 2.62; N 2.80; CI 43.26. The content of epoxy groups is 8.40%.

The structure of compounds (1a-IVa) was confirmed by physico-chemical methods, and also by a counter-synthesia. IR-spectra of compounds (1a-IVa) show absorption bands at 850, 920 and 1265 cm^{-1} which are characteristic of epoxy group.

The purity of initial and synthesized products was checked by a thin-layer chromatography according to the known method[7]. The procedure of kinetic measurements and treatment of experimental results have been described in the previous papers[5-9].

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